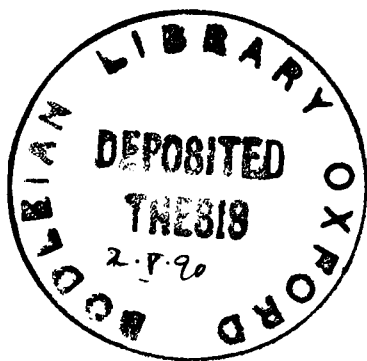


CORRECTIONS TO D.PHIL THESIS.

- Page 15 Equation 2.1 N_A = Avogadro's number = 6.023×10^{23}
- Page 61 Equation 4.12 L = thickness of substrate, $n_s^{w,2w}$ = refractive index,
 $f_s^{w,2w}$ = angle of incidence in the substrate.

THE PREPARATION AND
CHARACTERISATION
OF NOVEL ORGANO-RUTHENIUM
LANGMUIR-BLODGETT
FILMS



By

Tim Richardson
New College
Trinity Term 1989

A THESIS
SUBMITTED FOR THE DEGREE OF
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ABSTRACT

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In recent years, there has been considerable interest in media which exhibit significant non-linear physical properties. The non-linear optical response of many materials has attracted a great deal of attention from the telecommunications industry owing to their possible use for signal processing applications. Also, applications such as thermal imaging depend ultimately upon the proficient operation of the active material within the device structure. Traditionally, inorganic materials such as lithium niobate and strontium barium niobate have been used for non-linear optics and infra-red detection. However, the last decade or so has exposed the potentially high efficiency offered by organic materials which, coupled to the ability to engineer their physical properties by subtle modifications at the molecular level, suggests an exciting and productive future.

In order to maintain compatibility with existing integrated optics and display technologies, it is often useful to process the active compound in thin film form. The stringent symmetry requirements imposed upon the molecules and their organisation in the macroscopic structure necessitates the existence of non-centrosymmetric molecular structures for second-order non-linear applications such as those mentioned above. The Langmuir-Blodgett deposition technique enables such assemblies to be constructed by the sequential transfer of organic monomolecular layers from a liquid-air interface onto a solid substrate. The precise control of film thickness and molecular architecture afforded by the technique allow polar multilayer structures to be produced which possess the properties required for highly efficient second-order non-linear physical operation.

This thesis describes the development of a series of novel organo-metallic complexes which possess the necessary molecular properties for LB deposition in addition to those required for the observation of a large non-linear response. The complexes offer substantially improved thermal stability over other LB materials, and are thus appealing to the industrial device engineer. Their physical properties have been systematically studied and related to their detailed molecular structure. In particular, optical second-harmonic generation studies have shown that they possess high molecular coefficients and have provided a launching stage for further development. Their high pyroelectric response has attracted much enthusiasm from both industry and academia because of their potential commercial exploitation in thermal imaging devices.

Acknowledgements.

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Finally, I think of my wife and our parents whom I thank sincerely and with affection. The written words of a scientist cannot do justice to their loving contribution.

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CHAPTER 1

Introduction.

1.1 Background.

Many organic compounds possess interesting electrical, optical and biological properties which can be utilised in a myriad of exciting applications such as thermal imaging [1], electro-optic modulation [2] and chemical sensing [3]. However, often the desired material characteristics exhibited at a molecular level are not transferred to the bulk macroscopic structure so that the expected physical response is not observed in practice. For instance, many molecules possess the necessary molecular features to double the frequency of laser radiation but such optical second-harmonic generation (OSHG) [4] is observed relatively infrequently from single crystals owing to the adoption of symmetric crystallographic structures.

In many applications there is a requirement to deposit the material of interest in thin film form so that the layer is compatible with existing planar technologies. The growth of single crystalline material [5], including those centrosymmetric in nature, in thin film form using existing crystal growth techniques is very difficult and the resulting control of the thickness is relatively poor. The polymer spinning technique, in which the active molecules are embedded in a polymer host matrix, is one possible method of partially

overcoming the problems associated with crystal growth, although post-deposition electrical poling is essential if asymmetric polar structures are required. Also, it is possible to dope such a polymer host system with only a small proportion (<10%) of active molecules. Alternative techniques used to deposit thin organic films are evaporation [6] and sputtering although little control over film structure is possible. Clearly, a deposition technique is required which circumvents the difficulties mentioned above.

The *Langmuir-Blodgett* (LB) technique [7], which consists of the successive transfer of monomolecular layers from a liquid-air interface onto a solid support, enables multilayered organic thin films to be constructed with precisely controlled thickness and molecular architecture. The ability to prepare either centrosymmetric or highly polar molecular assemblies makes the process an extremely attractive technique to researchers in many scientific fields. In order to deposit organic films using the LB technique, it is often necessary to make modifications to the existing molecular structure of the materials of interest such as the substitution of a hydrocarbon chain to enable the molecules to float and align correctly on a liquid surface. Also, the thermal and mechanical stability of organic materials are often low and consideration must be given to methods of improving these features in order to increase the attractiveness of LB materials for commercial devices.

Much interest has been shown over the last decade or so in the non-linear physical properties of organic materials. In particular, a great deal of research has involved the study of the second-order non-linear optical response of conjugated organic compounds [8] since the realisation that such materials are potentially more efficient for processes such as OSHG and electro-optic modulation. Also, the research effort in organic pyroelectric materials [9] is gradually rising because of the possibility of obtaining novel, large-area thermal imaging devices at low cost. Both of these second-order non-linear physical phenomena rely critically upon the existence of polar, non-centrosymmetric crystal structures. Both fields of study would additionally benefit from the ability to prepare active

media in thin film format to achieve compatibility with existing integrated optics and display technologies.

This thesis is concerned with the development of a class of novel organo-metallic complexes for use with the LB technique and designed to perform the non-linear physical functions mentioned above. In particular the physical properties are related to the detailed chemical structure of the molecules in order to establish the necessary design criteria to allow more efficient molecules to be obtained.

1.2 Résumé of the thesis.

The thesis begins with a discussion of the LB technique itself and the associated research on novel materials. A brief introduction to the historical development of the subject is included in addition to a description of the wide variety of potential applications of LB films [10] which makes the field so interesting to work in. The different types of Langmuir trough and modes of deposition are explained to give the reader an awareness of the capabilities of the technique.

Chapter 3 is concerned with the non-linear physical properties of organic materials which have been investigated during this work. Particular attention has been given to OSHG and pyroelectricity. The observation of both effects is critically dependent upon the arrangement of non-linear molecules in polar, non-centrosymmetric macroscopic structures. The physical origin of OSHG is detailed and the materials that have been researched for this application are discussed. The potentially high efficiency of organics is stressed and related to their molecular features such as electronic conjugation and the presence of electron donating and withdrawing chemical groups. Finally, a discussion of the applications of highly optically non-linear materials is given. The nature and mechanistic origin of pyroelectricity in organic materials is much less well-understood.

However, the phenomenon itself is explained and shown to be an essential area of research for the important application of thermal imaging.

The following chapter describes in detail the main experimental techniques that have been used to characterise the materials studied in this research. They include uv-visible absorption spectroscopy [11], quartz microgravimetric studies [12] and several structural techniques [13]. Electric field induced second-harmonic generation (EFISHG) [14] has been extensively used to characterise the second-order optical non-linearities of many of the organo-ruthenium complexes. The apparatus used is described and the practical derivation of the non-linear coefficients is explained. Second-harmonic generation from solid LB films has also been researched and the relevant experimental details are presented. The thermal properties of the organo-metallic compounds, including their pyroelectric response and, importantly, their thermal stability have been assessed.

Chapters 5 and 6 are concerned with the detailed characterisation of the organo-ruthenium complexes and their precursors in solution, Langmuir film and LB film form. The uv-visible absorption properties of the solutions of all the materials studied are presented in Chapter 5 and analysed in detail owing to their relevance to the optical non-linear response and to establish the relationship between molecular structure and spectral characteristics. This is followed by a description of the preparation of Langmuir layers of the novel organo-ruthenium complexes. Heterogeneous Langmuir films have been studied and, in particular, many interesting features have been exposed within a two-component system in which the ruthenium complex is mixed with its corresponding precursor. Chapter 6 details the properties of the transferred LB films and the optimisation procedures to establish the conditions for the most efficient deposition. The data collected from the characterisation experiments are analysed and, where possible, related to the molecular structure. Many interesting results have arisen from these experiments including the thickness determination using ellipsometry [15] and surface plasmon reflectometry [16].

Also included in this chapter is a study of the thermal stability of the bulk powders and the breakdown temperatures of LB films of several of the complexes. This relatively simple investigation has enabled much information to be gathered regarding the intermolecular forces at play. The lessons learnt from this investigation may be applied to future studies on new materials.

The last main chapter includes a description and analysis of the non-linear physical properties of the organo-ruthenium complexes and their precursors. It begins with the results of the non-linear optical characterisation of the precursor molecules using the EFISHG technique which has enabled estimates of the non-linearities of the ruthenium complexes to be made. This is followed by an account of experiments on second-harmonic generation in LB films of some of the materials. The most recently synthesised complexes exhibit large molecular hyperpolarisabilities which will be assessed in the future using the surface plasmon resonance technique. The pyroelectric properties of the organo-ruthenium complexes are also discussed and compared to other media such as spin-cast polymers and ceramics.

Finally, the results obtained from the work described in this thesis are summarised and conclusions drawn in order to allow suggestions for future research to be proposed.

CHAPTER 2

Langmuir-Blodgett Films.

2.1 Introduction.

The proficiency of the organic chemist of today makes it possible to modify the molecular structure of materials in a very precise and controlled manner. In this way, the interesting physical properties of organic compounds may be optimised so as to perform a particular function. For example, organic conductors and chemical sensing agents are presently receiving a great deal of attention as are heat-sensing and optically active organic materials. However, many of the corresponding physical properties lay unobserved owing to the structural restrictions imposed upon the material in its macroscopic form. For instance, most organics crystallise with a centre of symmetry, which means that second-order nonlinear phenomena, such as optical second harmonic generation (OSHG) and piezoelectricity, cannot be demonstrated even though one would expect to observe such effects on consideration of the characteristics of the discrete molecule. For many applications, it is also of paramount importance to be able to produce very thin ($< 1\ \mu\text{m}$), highly uniform organic layers. However, thermal evaporation, sputtering and spin-coating techniques do not possess this capability.

Clearly, there exists a great demand for a deposition technique which facilitates the production of well-ordered, thin film organic assemblies whose molecular packing and thickness may be precisely and accurately controlled. The only coating process which achieves this specification is the Langmuir-Blodgett (LB) technique [17], in which a compact floating monomolecular layer is transferred from a liquid-gas interface onto a solid substrate. The details of the procedure will be discussed later in this chapter. Firstly, however, it is instructive to briefly consider the historical development of the subject.

2.2 Historical Aspects.

The stilling of waves on a water surface by means of oil was known many hundreds of years ago. The Roman philosopher, Pliny [18], mentioned that this property of oil was used to advantage particularly by divers in order to allow more light to the bottom of the sea by reducing stray reflections from the surface. Bermudian fishermen also spread oil on the sea in order to see the fish more easily than when the surface was ruffled by the wind.

In the 18th century, the American politician, Benjamin Franklin [19], performed several simple experiments during his travels and was always struck by their dramatic outcome:

" This was the sudden, wide, and forcible spreading of a drop of oil on the face of the water. If a drop of oil is put on a polished marble table, or on a looking glass that lies horizontally; the drop remains in its place, spreading very little. But when put on water it spreads instantly round, becoming so thin as to produce the prismatic colours, for a considerable space, and beyond them so much thinner as to be invisible, except in its effect of smoothing the waves at a much greater distance. "

It was Lord Rayleigh [20] in 1899, however, who first suspected that the resulting thin layer of oil was only a single molecule thick. Despite this discovery, no further developments were made during the following two decades. But between the two World Wars, Irving Langmuir [21] extensively studied the behaviour of certain organic compounds when spread as monomolecular films on a water surface. Today, such layers are referred to as Langmuir films. He and his co-worker, Katherine Blodgett [22], extended the technique to encompass the successive transfer of Langmuir films onto solid substrates to produce "built-up" multilayered assemblies that are now referred to as Langmuir-Blodgett films. They showed how the deposition of such films was highly dependent upon conditions such as the pH of the water and the surface pressure and succeeded in preparing useful multilayered structures such as anti-reflection coatings for instrument panels and spectacles [23]. Their research and publications are eloquently described in a book by George Gaines Jr [24]. The advent of the Second World War curtailed their study of organic films and little work was done until a major resurgence of interest in their technique occurred in the 1970's. Since this time, the scientific community involved in research in this field has grown dramatically.

2.3 Basic Concepts of the Technique.

The basic requirement for the preparation of floating layers is a clean and enclosed water surface whose area may be continuously varied. Langmuir films are formed by carefully applying a solution of an appropriate material dropwise onto the water surface. If the correct choice of organic solvent has been made, the solution will spread forcibly over the surface and, after solvent evaporation, there will remain an evenly distributed layer of solute molecules. The classical materials that have been widely researched are the alkanolic acids. These molecules possess a hydrophilic acid group and a strongly hydrophobic long alkyl chain which protrudes from the water surface (Figure 2.1 a).

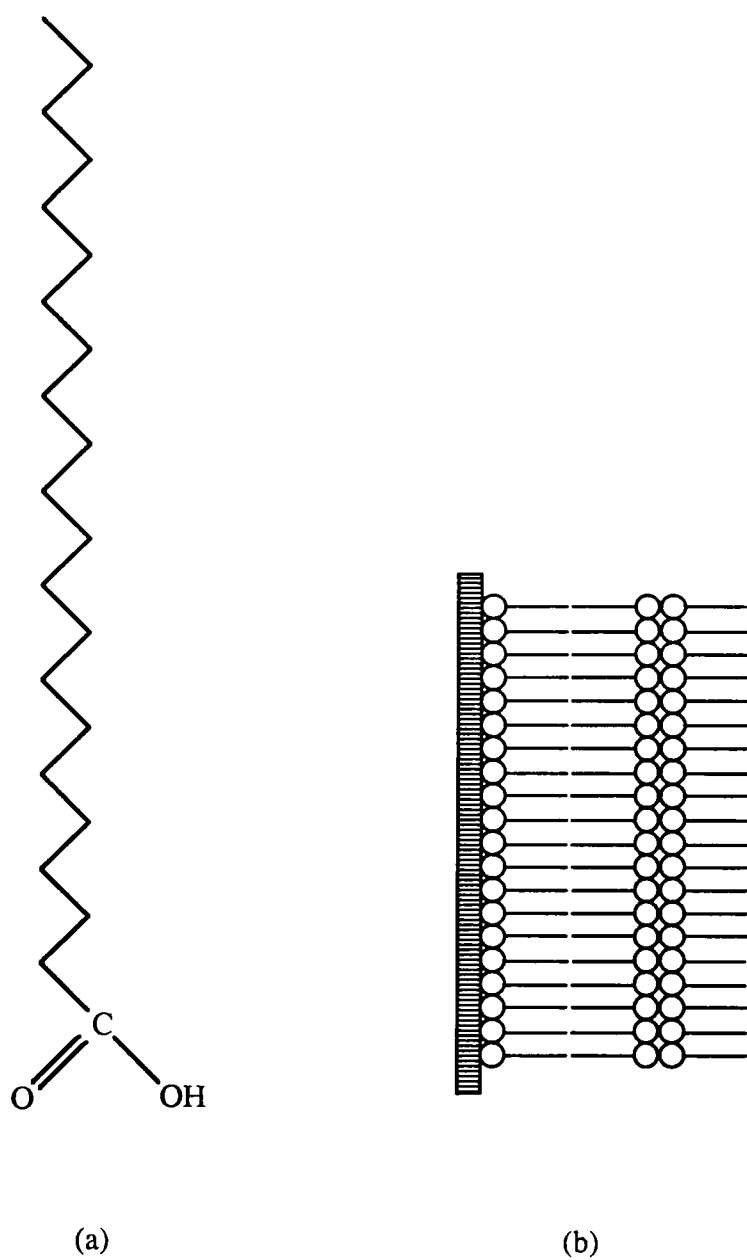


Figure 2.1: The molecular structure of (a) a behenic acid molecule and (b) the resulting Y-type LB multilayer structure.

If the area available to the layer is slowly reduced, the floating film is compressed and the molecules gradually approach each other more closely, begin to interact significantly and eventually align in an ordered manner as a quasi-two-dimensional "solid" phase. It is now possible to transfer this floating compact layer onto a solid by withdrawing a suitable substrate through the liquid-air interface. Indeed, further transitions of the substrate through the layer result in the deposition of subsequent layers of molecules and the formation of a multilayer organic structure (Figure 2.1). A detailed account of the deposition process will be given later in this chapter.

In order to obtain uniform coverage of a substrate, it is essential to maintain a constant surface pressure within the floating Langmuir film. This has been achieved by several methods. Langmuir and Blodgett [25] added a drop of oleic acid at one end of their trough. This was screened from the Langmuir film under study by a thin silk thread. The oleic acid was found to be composed of hydrophobic molecules which spread readily into the entire area available to them, and, in so doing, exerted a well-defined pressure on the monolayer. The excess oil remained in the form of small lenses on the water surface. As the surface pressure within the Langmuir monolayer decreased during transfer onto a solid, the lens-like globules expanded to fill in the newly-created free space on the water surface and to reattain the initial surface pressure. The oleic acid at one end of the trough therefore behaved as a compression piston for the Langmuir monolayer at the opposite end.

Modern deposition equipment incorporates sophisticated electronic feedback systems so that the barrier which defines the area available to the layer is motor-driven in direct response to variations in the surface pressure. The performance of such systems depends upon the amplifier gain in the feedback circuit and the geometry of the trough used. It is important not to restrict the fluidity of a floating

film by poor design of the barrier layout and improper surface pressure measurement.

The liquid subphase used almost without exception is water. It is vital that the subphase is as pure as possible as even the slightest levels of contamination can drastically affect the properties of most Langmuir monolayers. The inherent low cost of water and the advanced state of its purification technology coupled to its polarity make it the ideal choice for a subphase material. It is often necessary to dope the liquid with mono- or divalent cations to modify the deposition and stability properties of the monolayers or to add acid or alkali to alter the pH of the subphase. In all cases it is important to use highly pure compounds to reduce the risk of contamination.

2.4 Materials.

A material must possess several characteristics if it is to be successfully deposited using the LB technique. Firstly, it must be as insoluble as possible in the subphase material which, as mentioned previously, is virtually always highly purified water. Solubility in a suitable organic solvent which is itself immiscible with water (subphase) is essential. Commonly used solvents are chloroform, dichloromethane, toluene and to a lesser extent acetone. The molecules of the spread material must not aggregate otherwise a true monolayer may not be formed. The monolayer must be able to withstand compression to a surface pressure at which the closely packed molecules may be efficiently transferred onto a solid substrate.

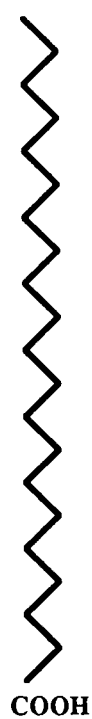
Ideally, the material should be amphiphilic in nature; that is, its molecules should have a hydrophilic, water-loving region and a hydrophobic part that protrudes from the water surface. These features enable such molecules to align in a highly orientated and well-ordered manner on the water surface. It is possible, however, to produce Langmuir and LB films of materials whose molecules lack

these characteristics [26], although the structure of such layers tends generally to be of poorer quality. Finally, it is crucial that the first monolayer is able to adhere to the substrate tenaciously and that the cohesive forces between adjacent layers in the multilayer assembly are strong.

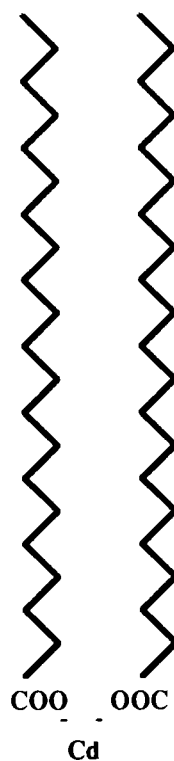
Relatively few of the numerous molecular and monolayer properties that need to be considered in detail to optimise deposition have been mentioned above. Monolayer rigidity, photostability and photo-oxidation are examples of others that must be examined. It is only possible in this thesis to describe the most important characteristics that affect the behaviour of a material and it is left to the reader to conjecture at the myriad of unrevealed properties that nature has produced.

The alkanolic acids and their derivatives possess all of the features required for compatibility with the LB technique, and have been widely investigated. The carboxylic acid head group is strongly attracted to the water but the long hydrophobic alkyl chain points away from the surface. Each molecule therefore lies in the same well-defined orientation relative to the surface of the water. The structure of behenic acid is shown in Figure 2.2 a . The lateral stability of the monolayer may often be increased by adding divalent cations, usually as a metal chloride, into the subphase which replace hydrogen ions in the carboxylic acid groups of two neighbouring molecules to form the metal salt as shown in Figure 2.2 b .

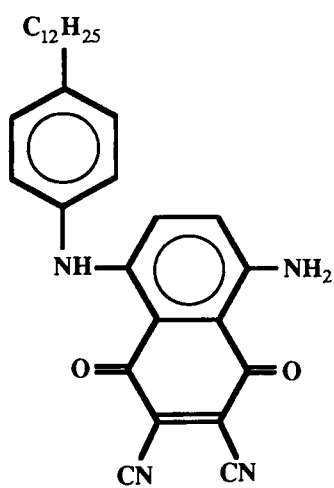
Replacement of a terminal -C-C- single bond along the backbone of a fatty acid molecule by a -C=C- double bond modifies the behaviour of the derivative on the water surface and on the solid substrate. Indeed, a great deal of research has been carried out on such materials owing to their potential use in electron beam lithography [27]. Adjacent molecules may be cross-linked as the double bonds can be opened upon exposure to the electron beam. It is then possible to selectively etch



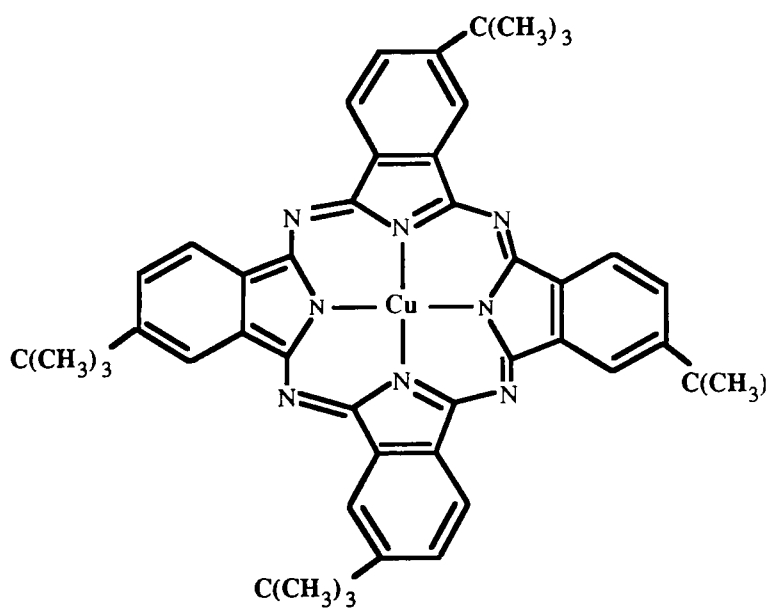
(a)



(b)



(c)



(d)

Figure 2.2: The molecular structure of (a) behenic acid, (b) cadmium behenate, (c) a naphthaquinone dye and (d) a copper phthalocyanine derivative.

away the unpolymerised regions of material and to subsequently perform the required processing to the exposed substrate.

Diacetylenic acids [28] are another interesting class of fatty acid derivatives in which carbon - carbon triple bonds have been substituted for two of the single bonds in the alkyl chain. Again, polymerisation is possible and their photolithographic properties have been studied.

Many aromatic compounds are of great interest optically and electrically, although they seldom form Langmuir monolayers owing to solubility in water or collapse at very low surface pressures. Their behaviour on the subphase may often be modified, however, by the substitution of long alkyl chains or by mixing with fatty acid molecules to reduce the solubility in the water, although the resulting LB films are thermally stable only to relatively low temperatures (60°C). Several classes of stable materials have been discovered, such as the azamethine dyes and the phthalocyanine dyes, and studied for ablative optical data storage [29] and gas-sensing [30] applications respectively, although the film quality is relatively poor unless the molecules are embedded in a fatty acid matrix (Figure 2.2 c,d).

This thesis is concerned with the characterisation of a novel series of complexes based upon highly stable organo-ruthenium compounds. It is possible to form reproducible quality LB multilayer films of such materials with only relatively short alkyl substitution. It will be shown that the complexation of an organo-ruthenium head group to a wide range of nitrile-terminated aromatic compounds enables completely novel Langmuir and LB films to be investigated even though it is generally impossible to form LB layers using the unsubstituted nitrile precursors alone.

2.5 The Langmuir Layer.

The study of the floating film on the subphase is an essential part of understanding and characterising the thin film properties of a material and, in particular, its suitability to the LB technique. Most importantly, it is possible to ascertain that the layer is indeed monomolecular upon examination of the area occupied on the surface and verification using molecular modelling techniques. The stability at the subphase-air interface may be readily assessed and the solubility of the layer and resistance to collapse when compressed are important parameters that need to be optimised.

The careful application of a solution of an organic material dropwise to the surface of a cleaned subphase followed by the subsequent evaporation from the surface of the organic solvent results in the uniform distribution of solute molecules in the form of an expanded Langmuir monolayer. Initially, the organic compound to be investigated is dissolved in an appropriate organic solvent. The necessary requirements that the solvent must satisfy, in addition to dissolving the material, are two-fold. Firstly, it must be immiscible with the subphase material otherwise some solute is carried into the bulk of the subphase during spreading. Secondly, it must have a moderate evaporation rate. A solvent that is extremely volatile will evaporate before efficient spreading has occurred leading to a non-uniform distribution of molecules across the subphase surface. In contrast, if the evaporation rate is very slow, the solvent will remain incorporated in the Langmuir monolayer and even the transferred LB film. Chloroform is the most commonly employed solvent which possesses the characteristics described above although dichloromethane, toluene, xylene and acetone are also encountered frequently. It is sometimes necessary to use a mixture of several solvents in the solution. For instance, a material may dissolve in only acetone, but addition of chloroform or toluene greatly improves spreading over the subphase surface. After solvent evaporation, the floating monolayer may be

manipulated. The detailed behaviour of a Langmuir film is critically dependent upon the nature of the particular compound used, but it is constructive to discuss the properties of an ideal monolayer-forming molecule such as behenic acid.

The area of the enclosed water surface can be continuously varied so that the region of space available to the floating molecules can be precisely controlled. In the expanded Langmuir film, the molecules are well-separated from each other and interact very little. This state can be thought of as a "gaseous" phase existing at the subphase-air interface and no change in surface pressure (π) is observed (Figure 2.3a). When the surface area is gradually decreased, however, the molecules are forced to approach each other more closely. This coincides with an abrupt change in surface pressure which continues to rise approximately linearly as the area is further reduced. This can clearly be seen in Figure 2.3b . Collisions between molecules occur more frequently and intermolecular forces, such as dipole-dipole and van der Waals' interactions, play a major role in determining the behaviour of the molecules on the surface. This state corresponds to a liquid-type phase in which the molecules are able to move considerably but not as freely as in the gas phase. Further compression of the monolayer results in another sharp transition in the surface pressure (Figure 2.3c). At this point and beyond, the molecules are tightly bound in a close-packed, "solid" layer, in which little rearrangement is possible. Eventually, no additional compression can be endured and the film undergoes collapse accompanied by a sudden fall in surface pressure (Figure 2.3d). The π - area isotherm allows the area occupied by each molecule on the water surface to be measured. The concentration and volume of the spreading solution are accurately known, so that it is straightforward to calculate the number of molecules in the monolayer. A simple division into the total area occupied by the monolayer (Equation 2.1) enables a value for the molecular area to be derived which may be compared to the value obtained from molecular modelling techniques. As a result,

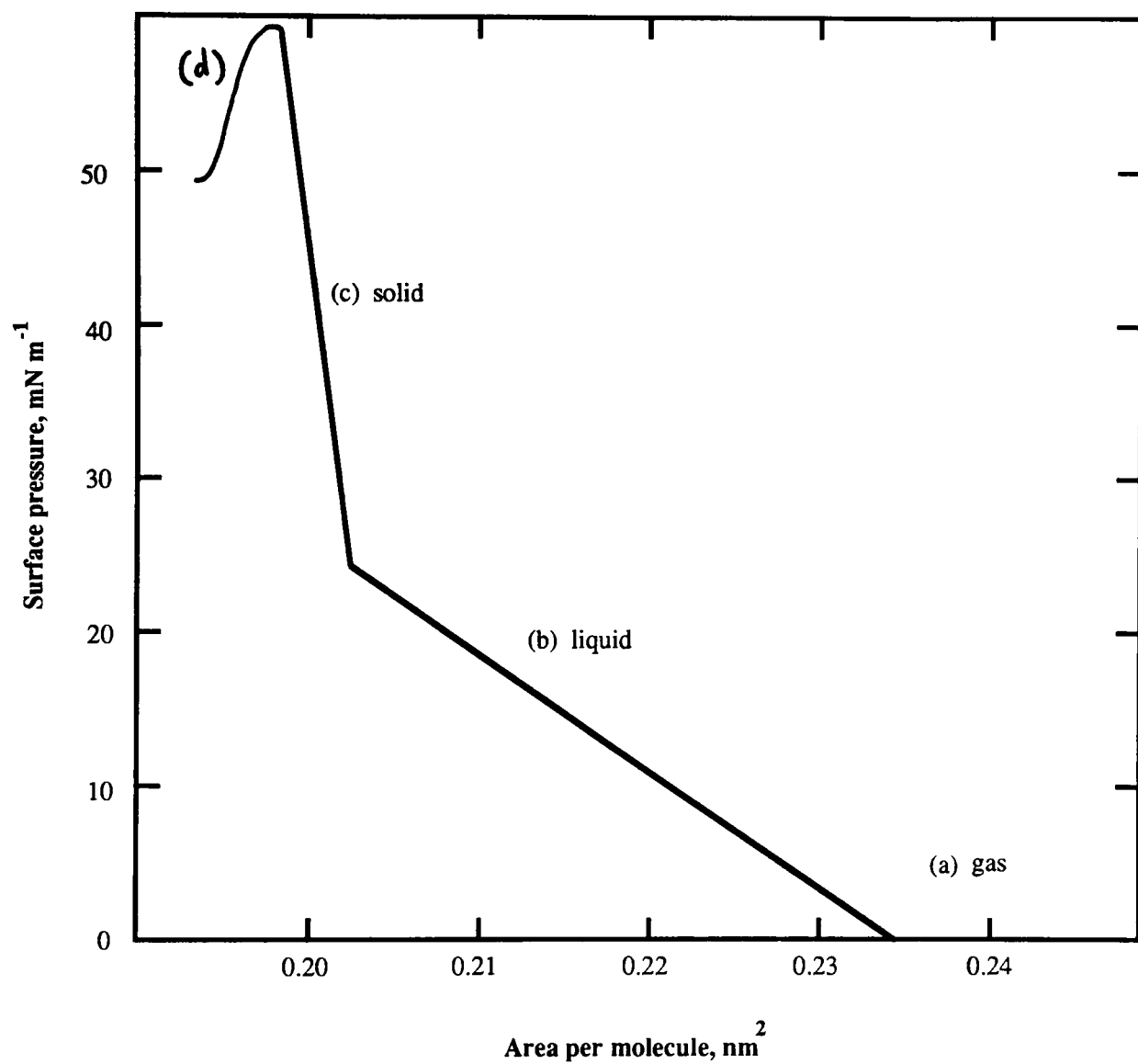


Figure 2.3 : Surface pressure - area isotherm for behenic acid monolayer showing (a) the gaseous phase, (b) the liquid phase and (c) the solid phase.

conclusions concerning the orientation of the molecules within the monolayer may be drawn.

$$A_m = \left[\frac{A_{Tot} M}{K N_A v} \right] \quad (2.1)$$

where A_m = the area per single molecule on the subphase surface (nm^2), A_{Tot} = the total area occupied by the floating film (nm^2), M = the molecular mass of the compound, K = the concentration of the spreading solution (g l^{-1}) and v = the volume of solution spread onto the subphase (l).

An important property of the monolayer which must be assessed in order to establish its worth for deposition purposes is its stability at the air-water interface. The area occupied by the monolayer on the surface can be monitored as a function of time with the surface pressure held at a constant value. The fatty acids are extremely stable displaying area losses of as little as 0.4 % per hour. The areal decay occurs owing to the occurrence of several processes. The major contribution arises as a result of dissolution of some of the molecules within the monolayer into the bulk subphase. Molecular reordering occurs initially after spreading and compression which also adds to the observed reduction in area. Other factors, although almost negligible, are evaporation from the monolayer itself and adsorption onto the solid surfaces in direct contact with the film.

It must be stressed that many materials behave differently to behenic acid when spread as monomolecular layers. For instance, some compounds do not show a distinct three phase surface pressure - area isotherm but a gradual increase in surface pressure is observed with no sudden phase transitions. In addition, few materials exhibit such a low area loss per unit time as the fatty acids. Typically, an area decrease of 2 - 3 % per hour is encountered.

2.6 Langmuir-Blodgett Deposition.

In order to produce transferred LB layers, a suitable substrate such as aluminium oxide or a glass slide, is normally moved vertically through a "solid" Langmuir film at the subphase-air interface. The surface pressure at which monolayers are deposited is dependent upon the particular material studied, but typically, values in the range $18 < \pi < 35 \text{ mN m}^{-1}$ are used. Figure 2.4a,b,c depicts the transfer process for a carboxylic acid. Hydrophilic substrates are lowered into the water before the Langmuir monolayer is spread and compressed as no material is deposited on the first downstroke through a compact fatty acid film. It is important to remove the substrate at constant speed in order to maintain the uniformity of the deposited layer. As the withdrawal occurs, material is transferred in such a manner that the carboxylic head groups are bound to the hydrophilic substrate surface and the long hydrophobic alkyl chains point away from the plane of the surface at a near orthogonal angle.

As discussed previously, it is essential that the surface pressure of the Langmuir film is maintained at a constant value. Failure to do this results in the creation of excess space on the surface as material is removed. The monolayer then expands to fill the surface voids which leads to a dramatic decrease in surface pressure. Correspondingly, the molecular surface packing density reduces and further deposition leads to a non-uniform, graded density LB layer. A simple electronic feedback system, in which the voltage output from the surface pressure measurement device is used to control the position of the trough barriers, enables the surface pressure to be corrected and reset to its predefined value.

After deposition of the first monolayer, the surface of the coated substrate consists of a closely-packed, well-ordered array of hydrophobic alkyl chains.

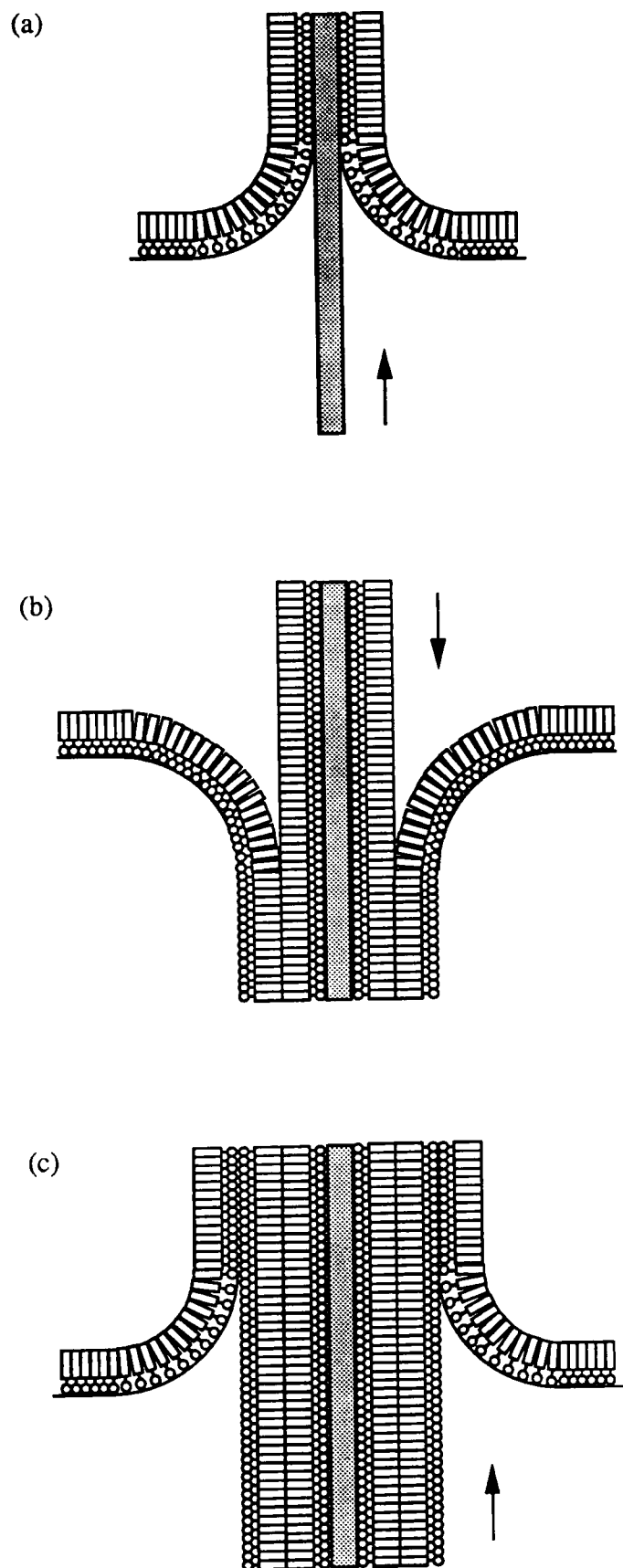


Figure 2.4 : The Y-type transfer process

Subsequent lowering of the substrate through the Langmuir layer (Figure 2.4b) results in the transfer of a second layer whose hydrophobic chains are attracted to those of the first LB layer. The attraction between the carboxylic acid headgroups causes the third layer to be deposited as the substrates moves upwards again (figure 2.4c). Further transitions across the interface enable monolayers to be successively deposited. A plot of the change in area occupied by the entire monolayer as a function of time during transfer onto a solid is shown in Figure 2.5 .

The process described above is known as Y-type deposition and results in an organic multilayered assembly of molecules whose structure is centrosymmetric (Figure 2.6a). Strictly, there always exists a small charge asymmetry due to the first monolayer, but molecular dipoles within subsequent bilayers are aligned with a centre of symmetry preventing the development of a large macroscopic polarisation.

However, as will be discussed later, several physical applications depend severely upon the presence of a non-centrosymmetric organisation of molecules. Some materials are not compatible with the Y-type procedure described above, but can only be deposited during a downstroke or only during an upwards excursion of the substrate through the floating layer. Such deposition is referred to as X- and Z-type respectively. The resulting structures of such multilayers are shown in Figure 2.6b,c in which the polarity is clearly depicted.

Another method of acquiring such asymmetry is to deposit two different materials alternately in an ABABA configuration. Several alternate layer trough designs now exist which allow monolayers of the two materials to be manipulated independently and polar multilayer structures to be prepared with no cross-contamination. Figure 2.6d shows the structure within such a multilayer. The dipole moment of material A is in the opposite direction, relative to the long alkyl chain, compared to that of material B. Consequently, when the monolayers are deposited

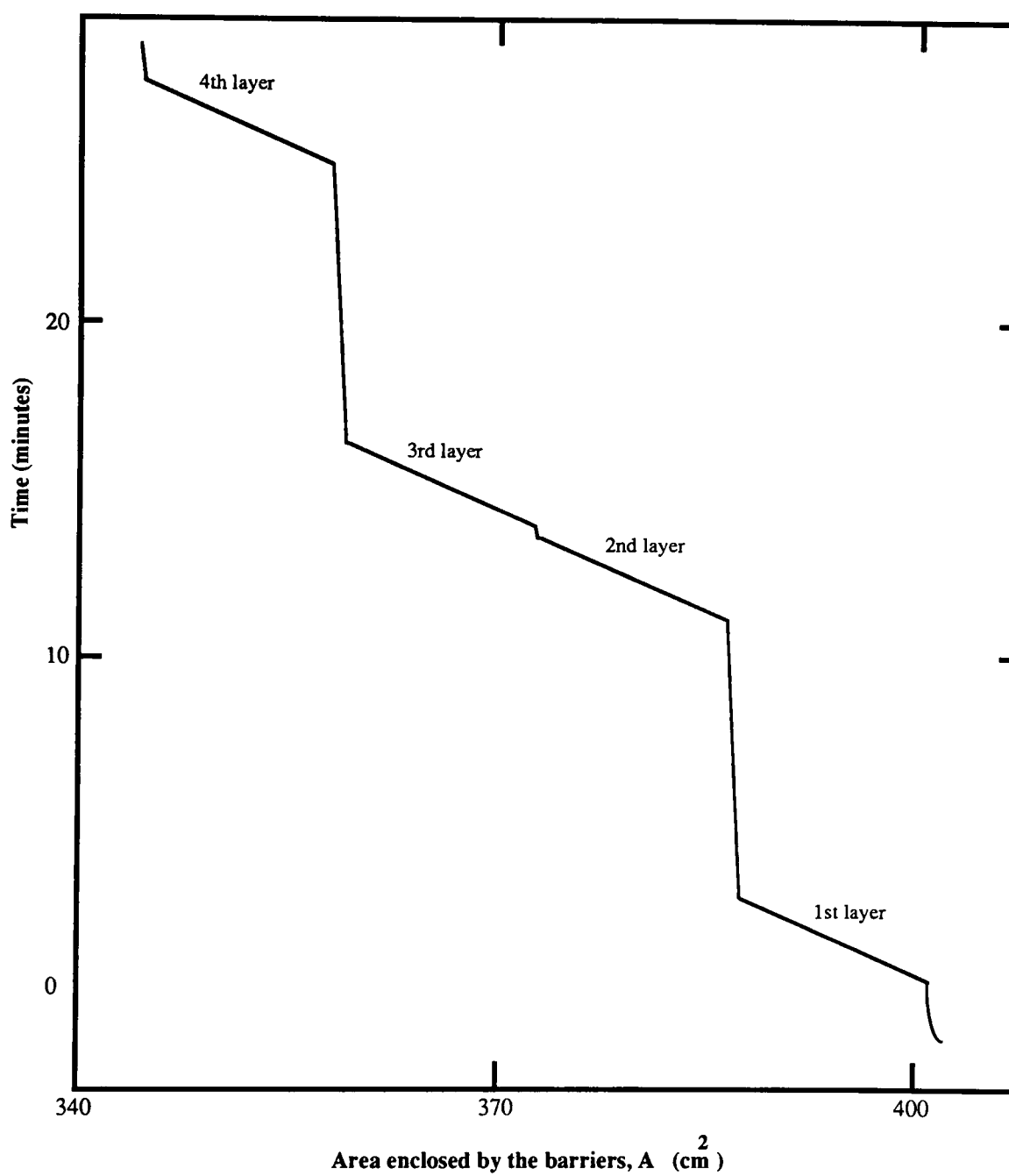
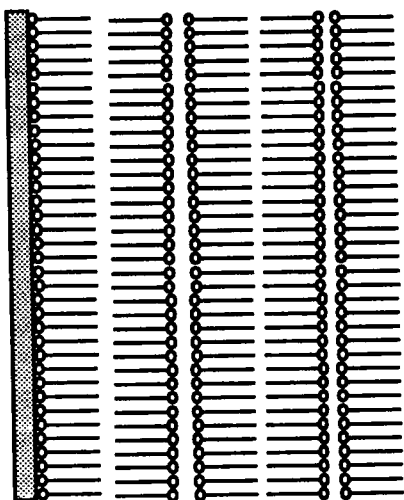
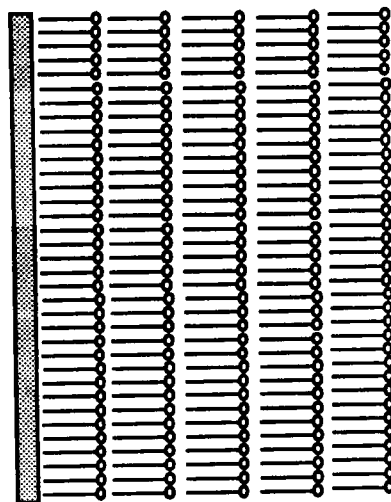


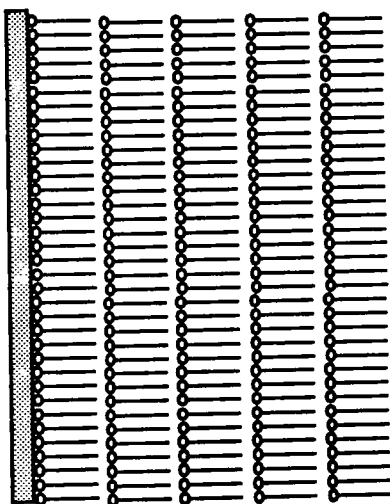
Figure 2.5 : The deposition of behenic acid in the centrosymmetric Y-type configuration.



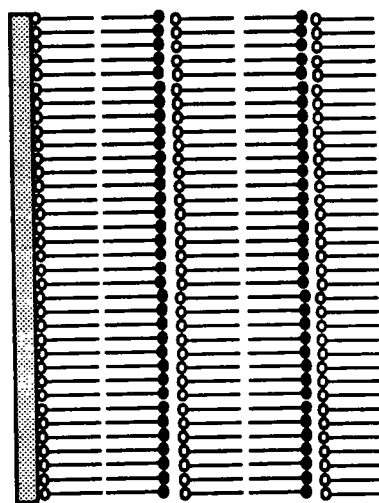
Y-TYPE
(centrosymmetric)



X-TYPE
(non-centrosymmetric)



Z-TYPE
(non-centrosymmetric)



**ALTERNATE LAYER
TYPE**
(non-centrosymmetric)

Figure 2.6 : The different deposition configurations that can be achieved using the Langmuir-Blodgett technique.

alternately, the dipole moments of both types of molecule are orientated in a single preferred direction so producing a large macroscopic polarisation although the alkyl chains adopt a pseudo-Y-type configuration.

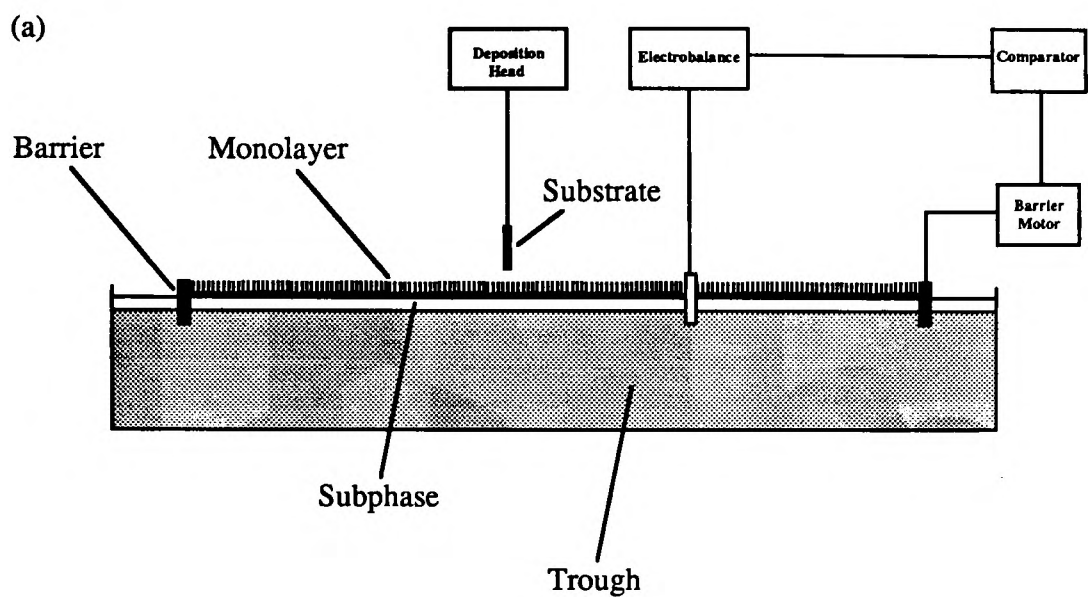
The resulting degree of control over the film thickness and molecular architecture is unsurpassed by any other technique. Indeed, the thickness is effectively quantised in units of a single molecular length although this parameter may itself be altered by the addition or subtraction of certain chemical groups.

2.7 LB Deposition Apparatus.

In this section the equipment used by the author to produce Langmuir and LB films will be described. Today, many different designs of Langmuir "troughs" exist in which the major variation is the geometry of the barrier system which defines the enclosed water surface. The conventional single layer trough will be discussed in detail followed by a description of the important features included in the design of the alternate layer trough. The instruments used at Oxford are of the constant perimeter design.

2.7.1 The single layer trough.

The single layer trough [30] basically consists of four sections: the water basin, the barrier system, the deposition mechanism and the control system. A photograph of the apparatus has been included as Figure 2.7 . The water basin is made from an inert PTFE derivative to reduce the risk of contamination of the subphase. Its depth is approximately 2 cm everywhere except around the central region where deposition would occur. The basin is moulded such that at the centre there is a deep (10 cm) well which can accommodate large substrates such as 3 inch



(b)

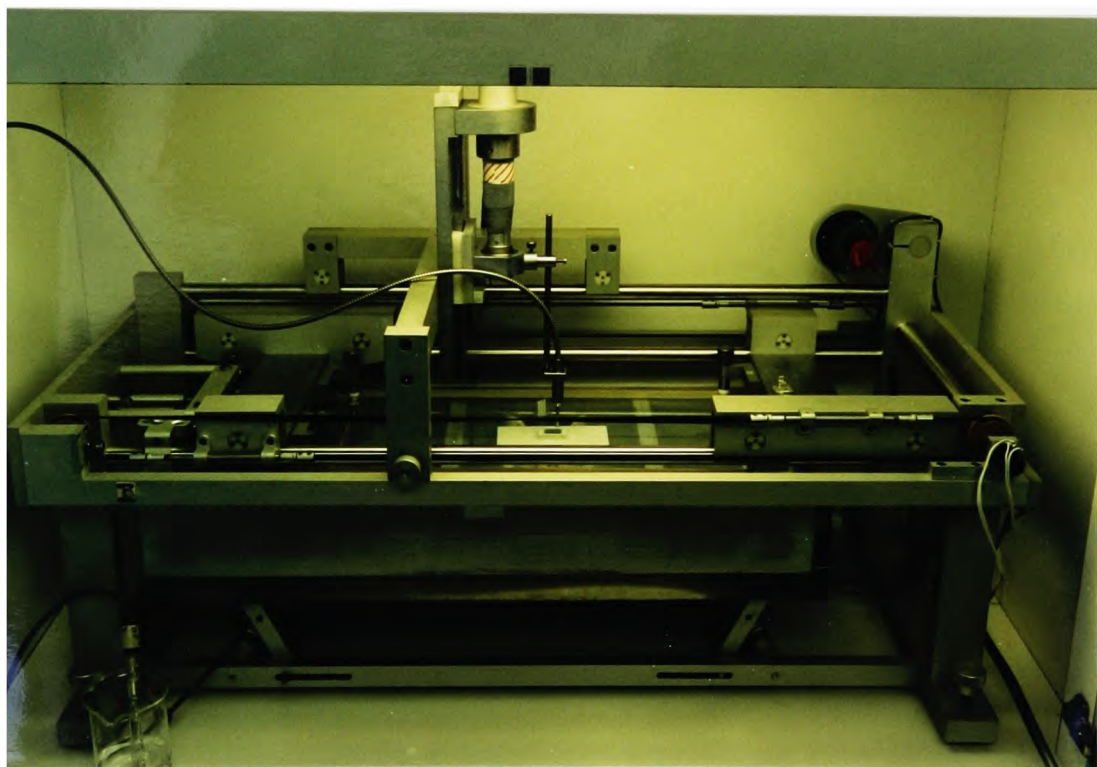
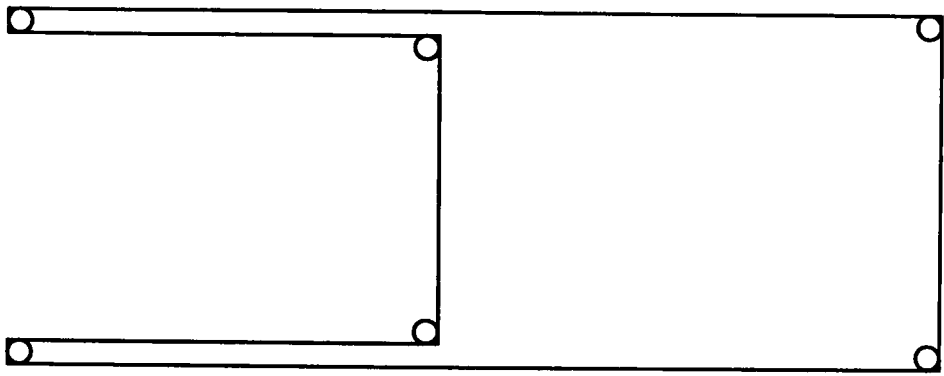


Figure 2.7 : The single layer Langmuir trough. (a) Schematic showing the main features and (b) a photograph of the trough in the Oxford laboratory.

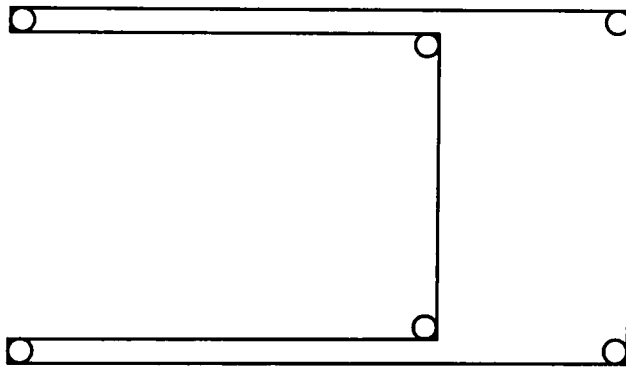
silicon wafers. This design allows large area coating to be performed but also minimises the volume of highly pure water that is required.

The barrier which determines the enclosed surface area in which the monolayer is confined consists of an inelastic "TeflonTM" coated fabric belt whose ends are bonded together to form a loop. It is fixed around six PTFE cylinders which hold it in position and enable it to slide easily as the enclosed area is changed. The level of the water is adjusted so that it lies at the midpoint of the belt although the exact positioning is non-critical. It is important to consider the stresses acting within the monolayer when it is compressed and to choose a barrier arrangement which minimises such forces. The actual geometry of the barrier is shown in Figure 2.8 for (a) large and (b) small confined surface areas. The shape of the barrier loop is governed by the position of two metal arms (Figure 2.7: A, B) which span the width of the water basin. Two PTFE cylinders are fixed to each metal arm such that when the arms are brought nearer to each other, the area enclosed by the belt is reduced. The arms are displaced via a motor-driven belt system visible in Figure 2.7. A high resolution potentiometer has been fixed to the drive shaft of the arms in order that the tapped voltage from the potential divider may be related to the position of the arms and therefore to the area of the enclosed water surface.

The deposition mechanism consists of a motor-driven micrometer onto which is fixed the deposition platform and substrate clamp. The speed of the insertion or withdrawal of the substrate can be accurately controlled by simply altering the supply voltage of the motor. Also, it is important to be able to define the limits of the excursion of the substrate through the Langmuir film so that specific regions of the substrate may be coated. The position of the barrier, the deposition platform and the excursion limits are all controlled electronically from a control box outside the Langmuir trough housing. During deposition, the surface pressure must remain constant and so the output from the surface pressure measurement system is



(a)



(b)

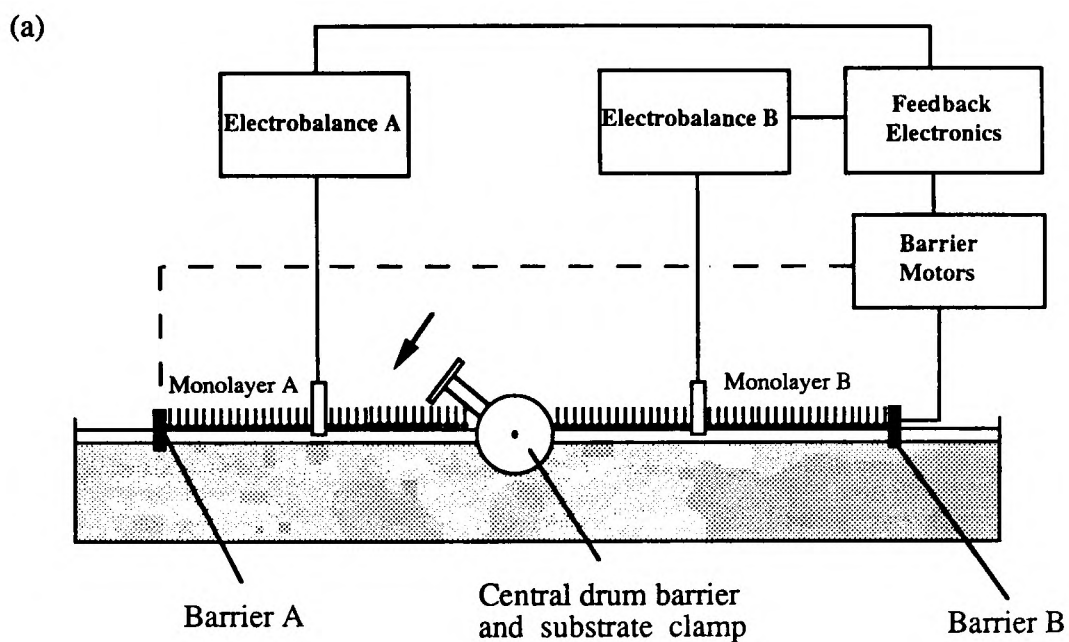
Figure 2.8 : The barrier geometry of the single layer trough with barriers
(a) open and (b) closed.

compared to the voltage preset on the control box and the necessary adjustment to the barrier position is made. The rate at which the area available to the Langmuir monolayer is reduced during the recording of a surface pressure - area isotherm can also be precisely adjusted.

2.7.2 The Alternate Layer Trough.

In order to deposit two different materials alternately, it is essential to be able to transfer the substrate on which monolayer A is spread to another supporting monolayer B. Several mechanisms exist but the rotary system developed in Durham [31] has been used in this work. The barrier consists of a continuous fabric belt, as in the conventional single layer trough, but in addition a central PTFE barrier divides the enclosed water surface into two independent halves as shown in Figure 2.9 . A circular drum, to which the substrate is clamped, is located at the midpoint of the central barrier. This is tightly fixed to a metal spindle axis which passes along the length of the barrier and which is driven by a geared-down motor. PTFE inserts are pushed up against the drum in order to maintain an effective seal between the two halves of the subphase surface. Care must be taken not to overtighten the inserts and therefore hinder the rotation of the substrate.

The area confined by the fabric belt and central PTFE barrier on each of its sides may be independently controlled from the external control box. Two surface pressure monitoring systems (Wilhelmy plate arrangement) are used in order that the optimum deposition surface pressures may be established for each monolayer even if the properties of both materials are very different. The speed of the substrate rotation may be precisely controlled by adjusting a potentiometer setting on the control box.



(b)

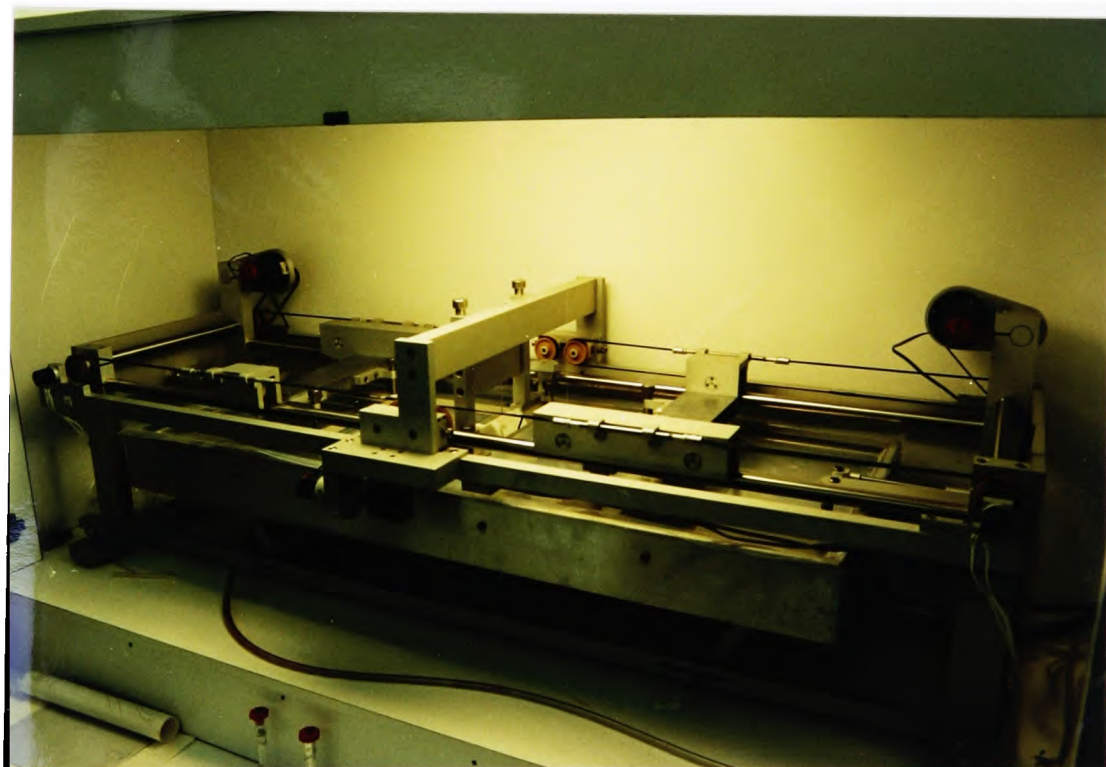


Figure 2.9 : The alternate layer trough. (a) A schematic diagram showing the independent halves each containing a different monolayer and (b) a photograph of the trough in the Oxford laboratory.

The change in surface area occupied by each monolayer can be plotted as a function of time during the deposition process. An idealised plot is shown in Figure 2.10 indicating that material is transferred to the drum as well as to the substrate. However, it has been shown that no cross-contamination occurs and that the deposition mechanism is reliable.

As mentioned previously, the alternate layer technique enables highly asymmetric multilayer structures to be prepared which are essential for the observation of second-order nonlinear physical phenomena such as electro-optic modulation and pyroelectricity. The availability of an alternate layer deposition system is a great advantage when working in this field. The procedures used in cleaning the LB troughs and substrates are detailed in Appendix A.

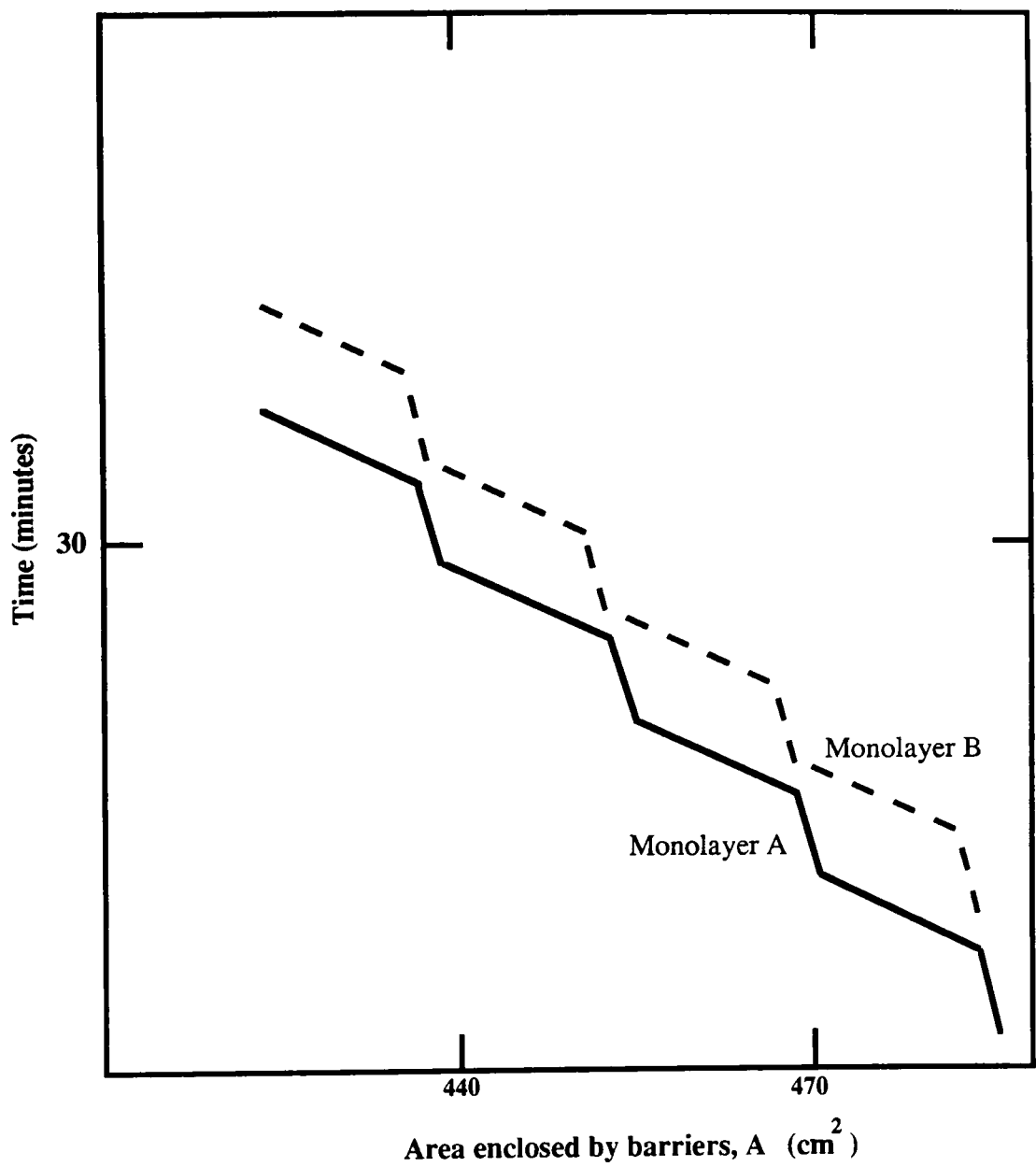


Figure 2.10 : An idealised deposition profile from the alternate layer trough.

2.8 Applications of LB Films.

2.8.1 Introduction.

The considerable surge of activity in Langmuir-Blodgett film research occurred about 40 years after the first detailed investigation of sequential monolayer transfer [32]. The initial motivation for this research arose from fundamental work by Kuhn [33] on energy transfer in monomolecular assemblies. The renewal of activity in university and industrial laboratories can be largely attributed to British and French research groups exposing the potential applications in the fields of electronics and optics [34]. Langmuir and Blodgett themselves, however, filed many patents including those about thickness gauges and anti-reflection coatings although none were developed commercially. An extensive review of the plethora of possible uses of LB films has been written by Roberts [35]. The different areas of interest are outlined below.

2.8.2 Model systems for fundamental research.

The Langmuir film technique provides a method of preparing simple artificial systems of co-operating molecules onto a solid substrate. Kuhn and his co-workers investigated the several different types of energy transfer that can occur between two dye monolayers separated by an inert fatty acid spacer layer whose thickness was varied in order to examine the effect upon the spectral characteristics [36]. This elegant work inspired several researchers in various physical sciences to transfer their skills into the novel and quickly developing LB film arena.

It is often possible to add divalent cations into the subphase which may, under the correct conditions, be taken up by the floating monolayer and transferred (as a salt) onto a substrate. This property has interested researchers because two or three-dimensional

arrays of ordered metal ions, such as Cd, Ba and Mn, may be obtained and used for dilute, standard radioactive sources and magnetic monolayers [37].

Much work is also in progress to study artificial biological systems on a Langmuir trough. Phospholipids, for example, form excellent quality bilayers on a water surface (as they do in nature in most cell membranes) and can be impregnated with proteins and enzymes. The ability to study the Langmuir layer with a wide range of experimental techniques has enabled several workers to delve into the complex biological intricacies of such membrane behaviour.

2.8.3 Passive thin film applications.

LB films may find applications in many applied areas of traditional interest to the industrial chemist such as adhesion, encapsulation, catalysis and the prevention of corrosion. However, the organic synthetic chemist now realises the potential market in areas such as electron beam lithography, magnetic tape lubrication and passive device modification.

(i) Electron beam lithography.

The desire for faster and increased memory storage capacity has induced much interest in further refinement of microlithographic techniques in order to produce ever-smaller circuit elements. The need for sub-micron resolution has necessitated a move away from conventional photolithographic methods to techniques involving X-rays and electron or ion beams [38]. Scanned electron beams are attractive owing to their excellent focussing properties that may be utilised. It is, in principle, possible to focus an electron beam spot to less than 10nm in diameter although electron scattering around the point of impact leads to a secondary halo of much larger size. The resolution may be increased by using

extremely thin resists. The 1 μm minimum thickness obtainable using spin-coated polymers is usually unacceptable owing to the large number of pin-holes and the thickness variation. Therefore, the LB technique provides a novel method of depositing suitable materials with much thinner dimensions to aid in microstructure fabrication.

Many materials have been shown to be polymerisable including diacetylenes and long chain derivatives of vinyl alcohol and pentadienoic acid and several researchers have demonstrated the remarkable resolution that is possible using multilayers of simple fatty acid salts [39]. The most studied negative resist material is ω -tricosenoic acid [40] because of the high rate (0.5 cm s^{-1}) of deposition which may be used. Much work is required to find an optimum solution to the many factors that must be considered in the design of a microlithographic resist, although LB films offer enormous scope to the organic chemist and should enable suitable resists to be available before the next major breakthrough of device miniaturisation for integrated electronics.

(ii) Lubrication.

Even a single monolayer has been shown to drastically reduce static friction and therefore interest has been shown in using LB films to lubricate substrates such as meter jewelled bearings [41]. Lubrication and encapsulation are very important areas of research in the magnetic tape industry. A good permeability barrier protects the oxidised magnetic medium and a good lubricant reduces wear and tear as the tape moves across the magnetic head [42]. Work is currently in progress to design a material which meets both requirements. The enormous magnetic tape industry would present a great opportunity for LB films to break into the commercial marketplace.

(iii) Device modification.

LB films have been shown to be of great use in the modification and enhancement of existing operating devices [43]. For example, surface acoustic wave (SAW) devices are commonly used in signal processing applications as filters and delay lines. They are based on quartz or lithium niobate and contain complex inter-digital electrodes whose design determine the operation of the device and the conversion between electrical and acoustic energy on the piezoelectric substrate. For certain functions, the device substrate often contains additional aluminium structures or arrays of geometrical shapes. The accuracy of the device clearly depends on the uniformity of the substrate and the precision obtainable with the particular microlithographic techniques used. When exacting specifications are demanded (usually in the military sphere) it is desirable to fine-tune the characteristics of the device after fabrication and testing. This procedure normally includes the design of another mask and further photolithographic steps and is extremely costly.

The LB film technique can provide a more convenient solution. The propagation characteristics of the surface wave can be adjusted by depositing specified thicknesses of monolayers on different regions of the substrate [44]. The corrective coatings may be deposited in well-defined bands of precisely known thickness to provide the desired amount of phase or amplitude correction. Although this impressive work is potentially useful, there is only a limited demand for such specialised devices.

2.8.4 Electrical applications of LB films.

Much work in the late 1970's and early 1980's involved the use of LB films deposited onto semiconductor devices to modify their behaviour. Workers at Durham University have shown that LB films can be used to optimise the performance of electroluminescent cells and other electronic devices [45]. In addition, several researchers

are interested in the electrical conductivity properties of thin LB layers for electronic and chemical sensing applications [46]. The interested reader may refer to the literature for detailed descriptions of these studies.

2.8.5 Non-linear physical applications.

Organic materials often possess much larger nonlinear coefficients than the commonly used inorganic compounds [47]. Until recently, the only means of producing acentric organic structures, essential for the observation of second-order nonlinear effects, has been to grow single crystals. But most organics crystallise with a centre of symmetry rendering them useless for such phenomena. However, the LB technique enables highly ordered, polar assemblies to be prepared and has created many opportunities to take advantage of the exotic molecular properties of organic compounds.

Materials with large second-order nonlinear optical coefficients can perform such functions as frequency doubling, electro-optic modulation and parametric amplification. A large electric field applied across a suitable material changes its refractive index and therefore the propagation conditions of light travelling through it. An appropriate arrangement of polarisers enables the output intensity of the light to vary in sympathy with the applied electric field. Such modulation has obvious applications in the communications field.

Other quadratic nonlinear physical effects include piezoelectricity [48] and pyroelectricity. Many thermal detectors are based upon cadmium mercury telluride which behaves as a photon detector although extremely low temperatures are essential for its efficient operation. Interest is growing, however, in pyroelectric detection due to a broad-band spectral operating domain and room temperature operation. Their only disadvantage is their reduced sensitivity compared to photon

detectors although this is not too critical if the pyroelectric devices are aimed at the low sensitivity end of the market. Much research is currently in progress to characterise the pyroelectric properties of organic materials for thermal imaging applications [49]. Modelling of the material and device parameters associated with such applications has resulted in the conclusion that LB assemblies may well possess near optimum properties for efficient pyroelectric detection. For example, the optimum thickness for the most efficient operation of a pyroelectric device composed of an LB film is around $0.1\mu\text{m}$ which is easily achievable using the LB technique whereas, for ceramics, this thickness is about $5\mu\text{m}$ and is not possible to obtain ceramic films thinner than $10\mu\text{m}$. In addition, their low permittivity and dielectric loss mean that their figure of merit for device operation is higher than most polymer, single crystal and ceramic materials. Research is continuing at Oxford University in order to elucidate the mechanisms responsible for the observed pyroelectric response in LB films of several classes of materials. Their use in body-heat sensing for rescue operations and security and in night-vision military applications makes pyroelectric detection based on LB films an attractive commercial proposition.

2.8.6 Other applications.

(i) Optical data storage.

The field of optical data storage [50] has attracted a great deal of attention recently owing to the enormous commercial demand for increased data packing densities. The availability of small GaAlAs semiconductor diode lasers possessing adequate power and stability has accelerated the design and construction of the lightweight optical reading heads required by the technology. The recording and reading wavelengths have also been defined by these lasers, so that the major

challenge now lies in identifying materials which are suitable for either photochromic or ablative techniques.

The thinness and uniformity of LB films make them ideal candidates for the ablative hole burning process. Heard *et al* [51] have shown that azamethine and naphthaquinone dyes can be modified in order to optimise LB and ablation properties. On exposure to the laser beam, a pit is formed by a heat-induced flow process. With vacuum deposited metal films and spin-coated polymers, the displaced material often forms a large ring around the pit. However, very little debris is found when LB layers form the absorbing medium as only a very small quantity of material is relocated. Adjacent pits may therefore be produced at extremely small separations. In addition, the absolute absorption of the LB multilayer may be precisely tuned to minimise the laser power requirement and the contrast ratio between the pit and the surrounding unablated film.

(ii) Novel sensors.

The physical and chemical properties of many organic materials change considerably upon exposure to certain gases or chemical species in solution. The gas molecules or dissolved species are adsorbed onto the surface of the organic layer and absorbed within its bulk. Evaporated and spin-coated layers are relatively thick compared to LB films so that desorption from within the layer can be extremely slow. Baker *et al* [52] have shown how the electrical conductivity of certain phthalocyanine compounds increases dramatically when nitrogen dioxide gas is injected into the sample cell with a typical recovery time of typically 100 seconds.

A far more sensitive technique, however, is to deposit the LB layer onto a surface acoustic wave (SAW) oscillator [53]. The oscillation frequency is critically dependent upon the nature and areal density of the surface coating and is extremely

sensitive to any changes occurring within it. When gas molecules pass over the device, they are adsorbed onto its surface and absorbed within the bulk. The mass of the surface layer therefore increases which results in a modification of the surface wave propagation conditions and the oscillation period of the SAW device. Desorption occurs relatively quickly as the multilayer is so thin.

The LB material may be designed to react specifically to a particular gas although a much greater research effort is required to achieve the degree of selectivity required commercially. Many researchers have attempted to immobilise enzymes and proteins within a fatty acid monolayer in order to produce a highly specific sensing layer which can detect minute concentrations of species such as aqueous potassium ions in blood.

2.9 Summary.

In this chapter, the underlying principles associated with the Langmuir-Blodgett technique have been introduced. The material requirements have been stressed and details of the preparation of floating and deposited monomolecular films have been given. There are many potential applications of LB films; many of these have been briefly outlined in order to give the reader an idea of their use in modern technological areas.

CHAPTER 3

Non-linear Physics of Organic Materials.

3.1 Introduction.

In this chapter non-linear optical phenomena, such as second-harmonic generation and the electro-optic effect, are discussed. The features required by organic materials to exhibit large optical non-linearities are considered in detail and the importance of an asymmetric macroscopic structure is stressed for second-order applications. This is followed by a brief account of pyroelectricity which can be observed using many of the organo-ruthenium compounds researched in this work.

3.2 Non-linear Optics of Organic Compounds.

Non-linear optics is concerned with the interaction of electromagnetic fields to produce new waves with a different frequency, phase or other propagation characteristic. The recent upsurge of interest in non-linear optical phenomena has arisen owing to the realisation that many organic materials possess the necessary chemical structure to exhibit larger optical non-linearities [54] than the conventionally used inorganic materials such as potassium dihydrogen phosphate (KDP), lithium niobate and quartz. The expertise of the modern organic chemist makes it possible to tailor the non-linear properties of certain organic molecules by the careful selection of various chemical substituents. The detailed molecular characteristics required for large non-linear effects will be discussed in Section

3.2.5 . In this thesis, attention will be focussed upon the second-order non-linear properties of organic materials although third-order processes will be briefly mentioned.

3.2.1 Physical Origins.

The polarisation induced in a linear optical medium when electromagnetic radiation passes through it is linearly proportional to the electric field, E as shown in Figure 3.1a . However, for a general medium, this linear term is only the first of a series expansion of the polarisation, P given by:

$$P = P_0 + \epsilon_0 \chi^{(1)} E + \epsilon_0 \chi^{(2)} E.E + \epsilon_0 \chi^{(3)} E.E.E + \dots \quad (3.1)$$

where P_0 = the permanent polarisation present in the material, ϵ_0 = the permittivity of free space and $\chi^{(1),(2),(3)}$ = the first, second and third-order macroscopic non-linear susceptibilities. It is clear from Figure 3.1b that the relation is non-linear at large electric field strengths which are readily obtainable with high power sources such as Nd:YAG lasers. If we assume a sinusoidal electric field variation in the electromagnetic radiation emitted from the laser source given by $E = E_0 \sin \omega t$ where E_0 = the amplitude of the field, ω = the frequency of oscillation and t = time, then we can write:

$$P = P_0 + \epsilon_0 \chi^{(1)} E_0 \sin \omega t + \frac{1}{2} \epsilon_0 \chi^{(2)} E_0 (1 - \cos 2\omega t) + \frac{1}{4} \epsilon_0 \chi^{(3)} E_0 (3 \sin \omega t - \sin 3\omega t) + \dots \quad (3.2)$$

It is clear from this expression that it is possible to excite harmonic frequencies ($2\omega, 3\omega$) with a strong fundamental electric field (ω). This has been diagrammatically shown in Figure 3.2 . The sinusoidally varying E-field produces an asymmetric, non-linear response in the polarisation field (Figure 3.2a) which can be Fourier synthesised and shown to contain harmonic frequency components (Figure 3.2b). Therefore, a material

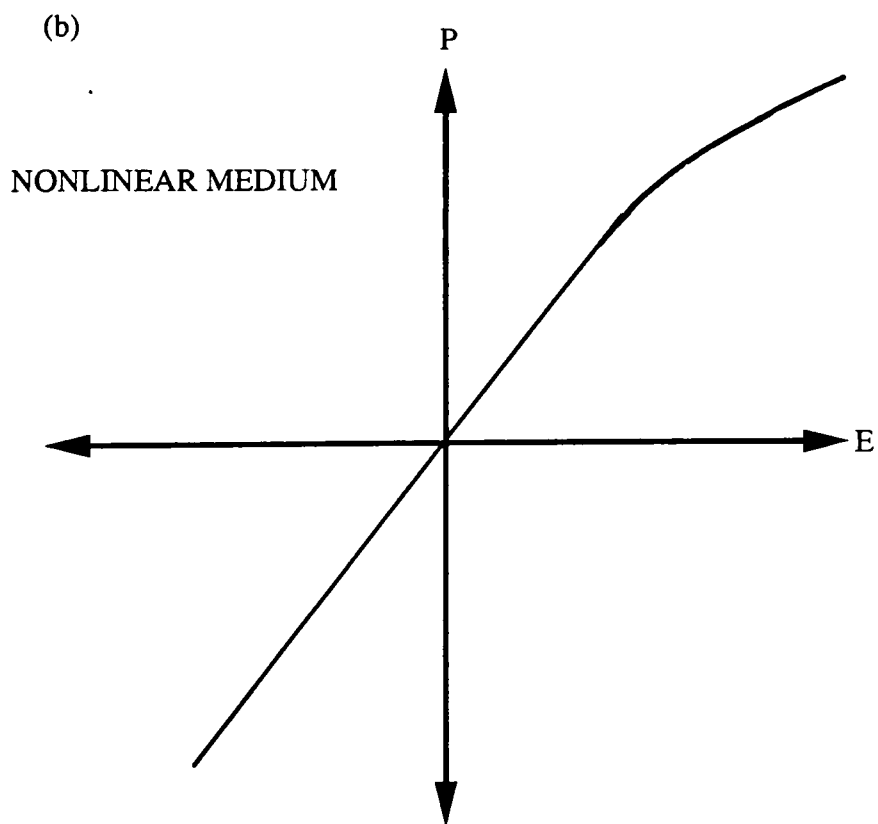
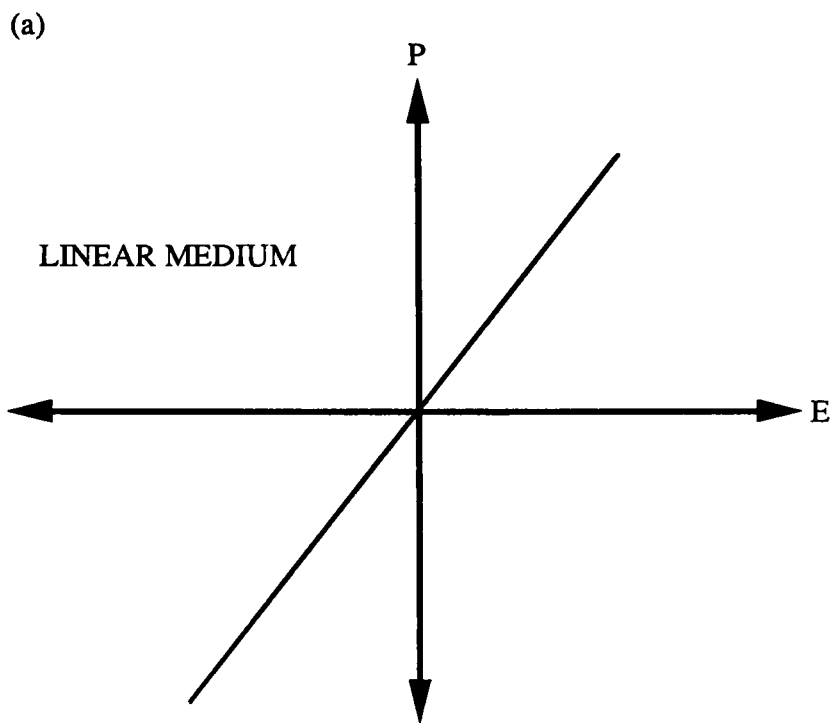


Figure 3.1 : The relationships between polarisation and electric field for (a) a linear optical medium and (b) for a non-linear optical medium.

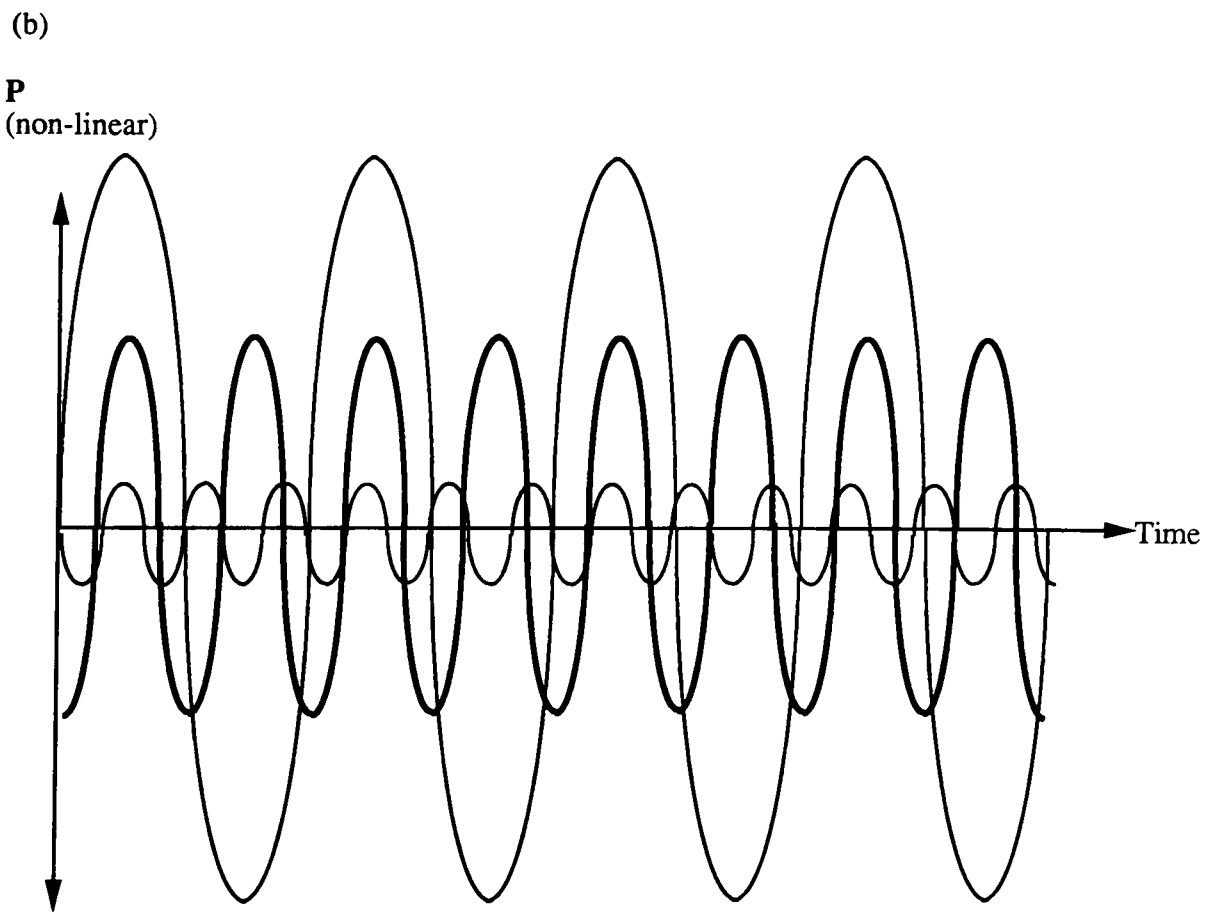
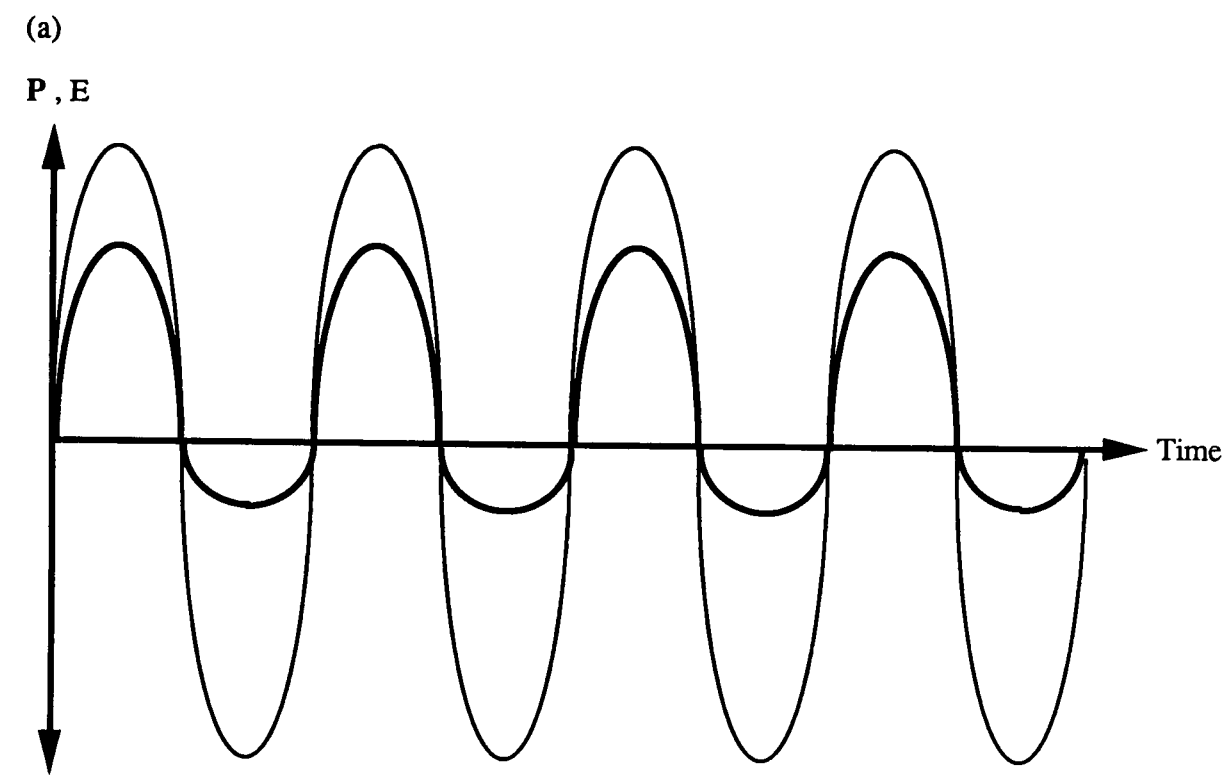


Figure 3.2 : The polarisation response of a non-linear medium showing the harmonic frequency contributions.

possessing a large $\chi^{(2)}$ value would produce a large second-order response and, in practice, a frequency-doubled output would be obtained. Similarly, a high $\chi^{(3)}$ would yield a frequency-tripled output.

The expression in equation 3.1 refers to a macroscopic structure in which the microscopic unit is an individual molecule for an organic material. It is sensible, therefore, to think of the non-linear response arising initially at the basic molecular level. Thus, the relation below may be written:

$$\mu = \mu_0 + \epsilon_0 \alpha \zeta + \epsilon_0 \beta \zeta \cdot \zeta + \epsilon_0 \gamma \zeta \cdot \zeta \cdot \zeta + \dots \quad (3.3)$$

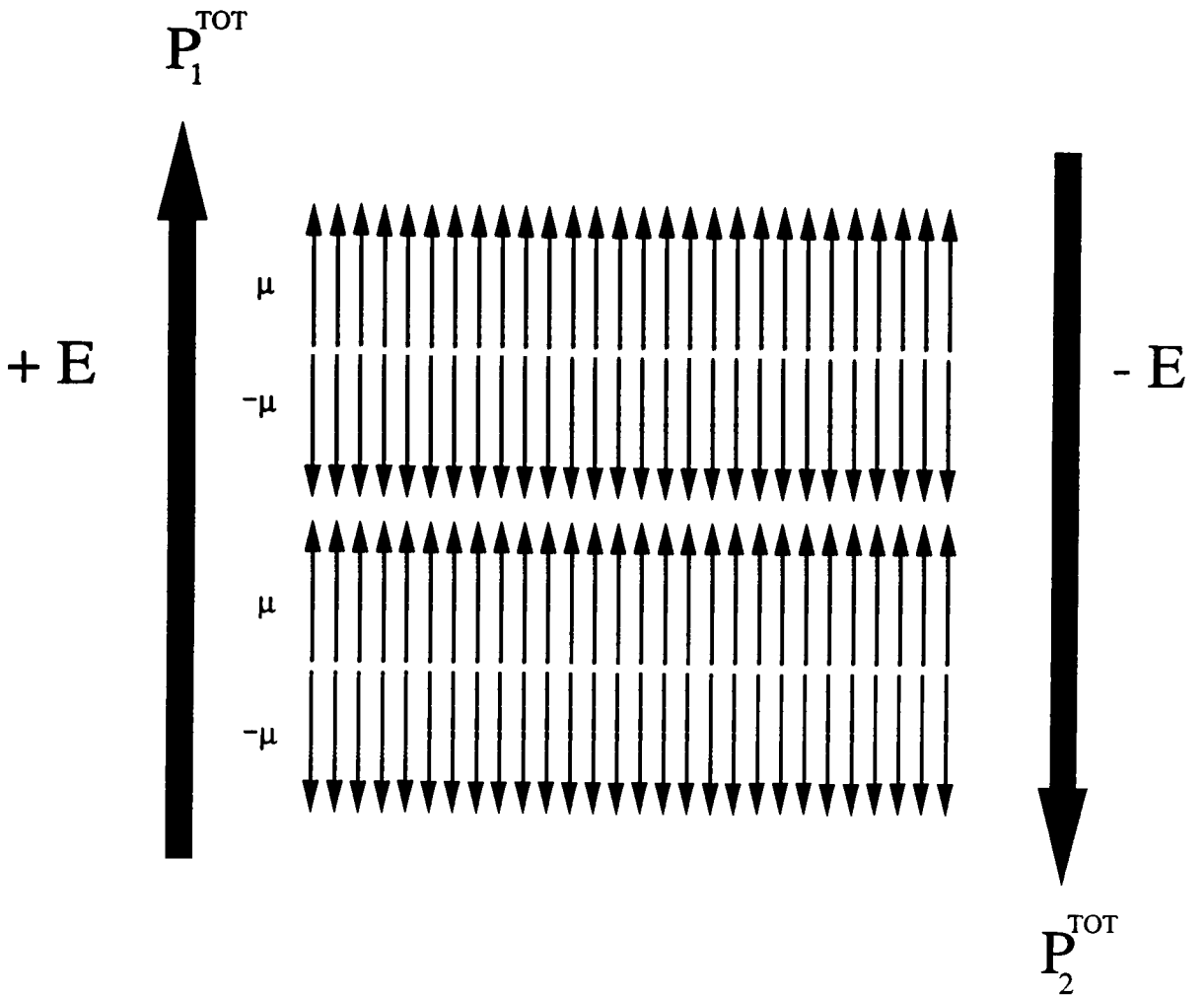
where α , β , and γ = 1st, 2nd and 3rd-order molecular hyperpolarisabilities, $\mu - \mu_0$ = the induced dipole moment and ζ = the local electric field acting on a molecule. The microscopic coefficients β and γ may be measured using the EFISHG technique [55] described in Chapter 4. The second-order hyperpolarisability, β , for example, indicates the size of the non-linear response for a single molecule.

3.2.2 Second-order processes.

From equation 3.1, it is evident that even order susceptibilities ($\chi^{(2)}$, $\chi^{(4)}$) vanish if the bulk material has a centrosymmetric structure (Figure 3.3). This imposes the most stringent restriction upon the choice of a suitable organic (or inorganic) compound for second-order non-linear optical applications. The relationship between $\chi^{(2)}$ and β can be described by a gas-orientated molecular model [56]:

$$\chi^{(2)} = N f^{2\omega} f^\omega \beta f(\phi) \quad (3.4)$$

where N = the number of molecules per unit volume, $f^{\omega, 2\omega}$ = local field correction factors and $f(\phi)$ = an orientation function which depends upon the crystal structure. Many



$$\frac{P_1^{\text{TOT}}}{\epsilon_0} = \chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \dots$$

$$\frac{P_2^{\text{TOT}}}{\epsilon_0} = \chi^{(1)} (-E) + \chi^{(2)} (-E)^2 + \chi^{(3)} (-E)^3 + \dots$$

If the medium is centrosymmetric, then $P_1^{\text{TOT}} = -P_2^{\text{TOT}}$ and $\chi^{(2)} = 0$

Figure 3.3 : Symmetry restriction for second-order non-linear optical phenomena.

organics crystallise with an inversion centre which renders them useless for second-order processes. Indeed, even the molecules of those organics whose crystal structures are asymmetric are often arranged in the lattice such that full advantage of the molecular non-linearity is not taken. In addition, it is difficult to grow single crystals in thin film form so that the structures are compatible with integrated optics technologies. It is clear that a technique is required which enables highly ordered and aligned, polar arrays of non-linear molecules to be deposited as a thin planar film. The LB deposition process possesses this capability as has been described in the previous chapter.

The efficiency with which the frequency of a laser beam is doubled by a material having a large $\chi^{(2)}$ is dependent upon several factors including the refractive indices of the fundamental and second-harmonic beams, the intensity of the incident laser radiation and the thickness of the material [57]. The second-harmonic output efficiency, η , can be expressed as:

$$\eta = \frac{32\omega^3 \pi^3}{c^3} \frac{\{\chi^{(2)}\}^2}{n_{\omega}^2 n_{2\omega}} z^2 I_{\omega} F\left(\frac{\Delta k z}{2}\right) \quad (3.5)$$

where $\eta = I_{2\omega} / I_{\omega}$ (in which $I_{2\omega}$ = the second-harmonic intensity and I_{ω} = the fundamental intensity), $n_{\omega,2\omega}$ = the refractive indices of the fundamental and second-harmonic waves, z = the thickness, and $F(\Delta k z/2)$ = a phase mismatch term. The theoretical derivation of this expression has been included in [reference 57](#) for reference purposes. For bulk single crystals several millimetres in width, the thickness dependence becomes extremely critical because of the phase-matching term which arises from the dispersion of the refractive indices $n_{\omega,2\omega}$ in the non-linear medium. Phase matching [58] may be achieved by several methods, the most common of which is angle phase matching. In this case, the launching angle of the fundamental beam can be arranged such that the refractive index of the fundamental balances that of the second-harmonic beam and a phase mismatch does not

occur as indicated in Figure 3.4 . The second-harmonic intensity is drastically improved when the phase matching condition is met. This expression is valid provided that the actual conversion of fundamental laser energy is relatively low so that there is no appreciable depletion of the fundamental power.

The thickness of LB films is so small that the phase mismatch term, given below in equation 3.6 tends to unity and a square law dependence is expected if the frequency-doubled output is plotted against the number of LB layers.

$$F\left(\frac{\Delta kz}{2}\right) = \frac{\sin^2\left(\frac{\Delta kz}{2}\right)}{\left(\frac{\Delta kz}{2}\right)^2} \quad (3.6)$$

Because of the thickness dependence of the frequency-doubled output, second-harmonic generation may be used to probe the structure [59] of materials deposited using the LB technique. The experimental details of the measurement are discussed in Chapter 4.

Therefore, it is clear that in order for a bulk structure to exhibit a large $\chi^{(2)}$ response, two criteria must be satisfied. Firstly, the discrete molecules themselves must possess the features required for second-order non-linearity, which will be discussed in section 3.2.6, and secondly, it is essential that they are arranged in the crystal lattice noncentrosymmetrically in order to take advantage of the molecular property.

There are three main methods of obtaining such asymmetry. The technology of crystal growth is well-advanced and can be used for the relatively few organics that possess acentric structures such as POM [60] and NPP [61]. However, the technique is not ideal because of its incompatibility with planar technologies and the small number of suitable materials. Another method is to dope a polymeric material such as PVdF with a non-linear dye. The mixed solution is spun-cast onto the substrate to produce a film of

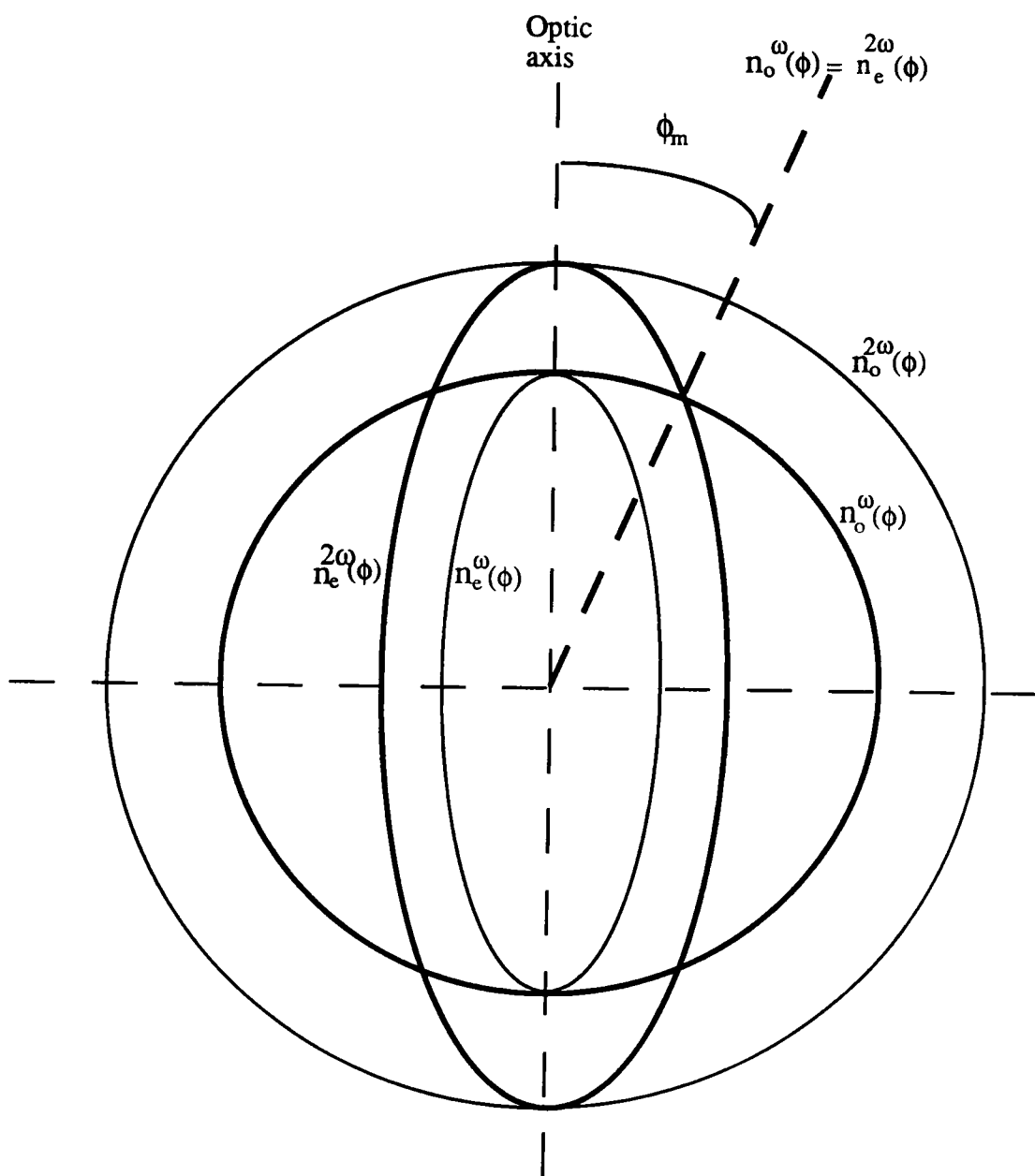


Figure 3.4 : Angle phase-matching in a second-order non-linear optics crystal.

typically 3 - 10 μm in thickness. In order to orient the dye molecules within the polymer matrix, a large poling electric field must be applied. It has been shown, however, that the resulting orientation is unstable and eventually reverts to a less well-aligned state, so reducing the macroscopic non-linearity. The advantages offered by the LB technique are numerous. Firstly, the advances made in organic chemistry allow a vast number of useful molecules to be chemically modified so that deposition is possible. Secondly, the floating and transferred layers are highly ordered arrays of densely packed molecules whose dipoles are preferentially orientated. Finally, the thickness and detailed molecular architecture may be precisely controlled to suit the particular device in question.

The various applications of materials exhibiting a large second-order response are discussed in section 3.2.6 .

3.2.3 Third-order Processes.

Reference to equation 3.2 shows that it is possible to obtain a third-harmonic term in the non-linear polarisation expansion. Generally, much less is known about the physical origins of third-order processes than $\chi^{(2)}$ phenomena, although much research is being carried out within this field because of the potential applications of materials displaying a high third-order response [62]. Optical bistability [63] is the most well-known in which the output laser power can occupy one of two states thus acting like a switch. Little will be said about this area of non-linear optics in this thesis as a different set of material requirements exist for third-order processes which are not necessarily (and usually not) satisfied by molecules having a large β coefficient.

3.2.4 A Comparison of Available Materials.

Most of the early pioneering work in non-linear optics concentrated on inorganic materials such as lithium niobate, potassium dihydrogen phosphate (KDP) and semiconductors which were all initially developed for other purposes such as piezoelectricity [64]. However, in the 1970's, a great upsurge of interest in organic compounds [65] occurred owing to the realisation that large second-order non-linearities were exhibited. In addition to this major advantage, it was also recognised that the number of subtle chemical adjustments that can be made to the molecular structure of an organic compound is enormously greater than for inorganics. Thus, the way was opened for a huge increase in the number of materials available for second-order non-linear applications.

Figure 3.5 shows the relative efficiencies of several classes of materials for second-harmonic generation and the electro-optic effect. The Miller's delta, δ , and polarisation optic coefficient, f , are figures of merit that define the potential use of a material. It is remarkably clear that organics easily surpass inorganic crystals such as ammonium dihydrogen phosphate (ADP). Indeed, further advances have been made in organics research in that several disubstituted azo compounds have yielded more than an order of magnitude improvement upon the figures of merit for 2-methyl-nitroaniline (MNA) [66]. The detailed characteristics of organic molecules that increase the second-order response will be discussed in the following section.

3.2.5 Optimisation of Organic Molecules for 2nd-order Non-linear Optics.

In this section, the characteristics of organic molecules that lead to a high second-order non-linear optical response will be discussed. It will be seen that it is possible to

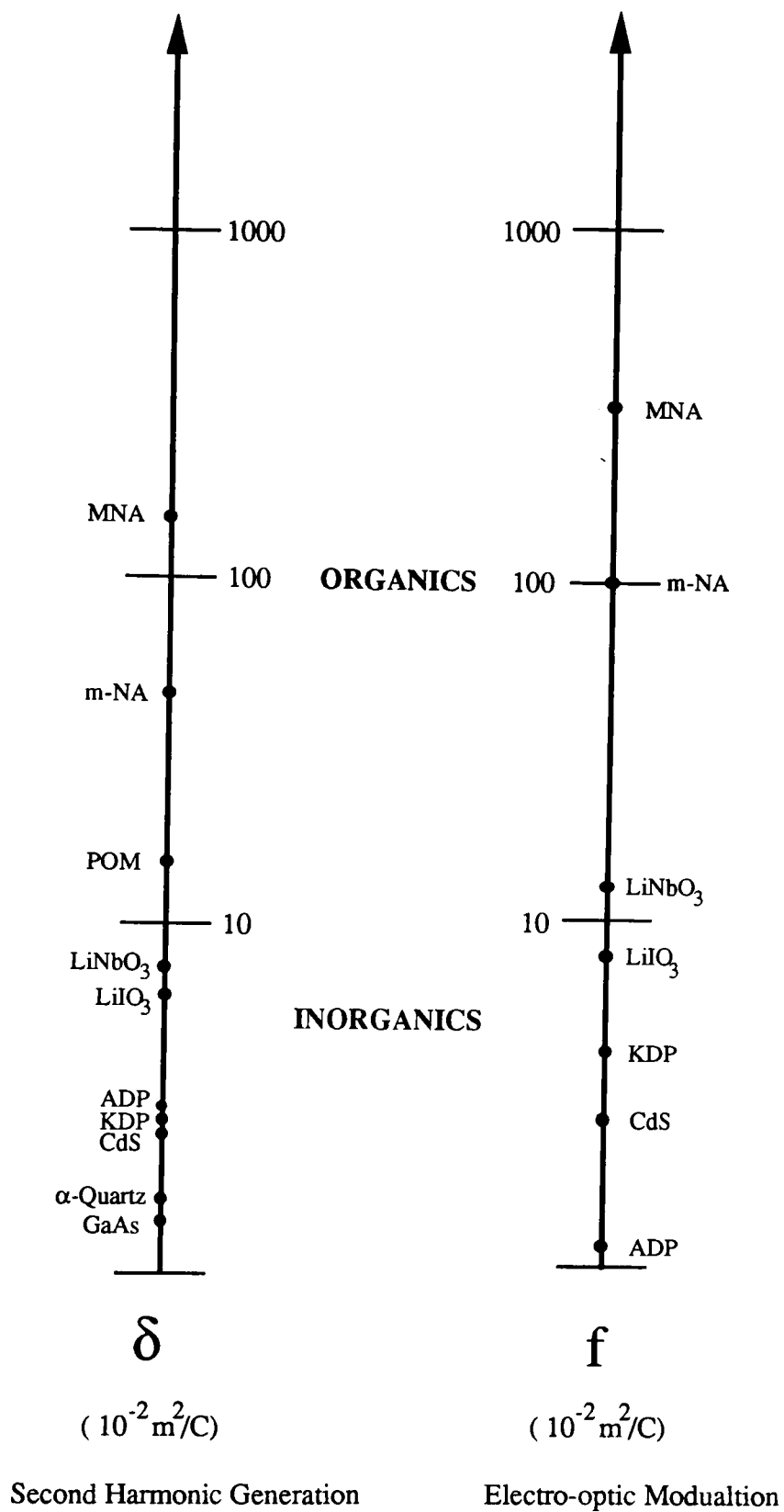


Figure 3.5 : Relative figures of merit for inorganic and organic materials for SHG and the electro-optic effect.

optimise the non-linearity of a given molecular system by choosing correctly the substituted electron donating and withdrawing chemical groups and the particular conjugated electron system.

It must be stressed that the ensuing account is written in terms of establishing a large molecular response. Some details are presented in section 3.2.5(ii) concerning the additional optimisation procedures necessary to induce non-centrosymmetric packing in a bulk single crystal. The Langmuir-Blodgett technique used in this work not only enables improved dipolar alignment within an asymmetric multilayer film (compared to bulk crystal growth) to be achieved, but it also reduces the complexity of the synthetic optimisation process.

The ultimate non-linear optical material must fulfil a plethora of requirements, some very general and others dictated by the particular application or device in question. The chemical points have been highlighted here, although one must not lose sight of equally important issues such as environmental stability, optical damage threshold, cost and the ease of chemical synthesis.

(i) Intramolecular Charge Transfer and Resonance in 2nd-order Hyperpolarisability.

The main difference between the electron systems of inorganic and organic materials is that the π -electrons of many organics are much more mobile than electron density in inorganics and, consequently, may be polarised relatively easily [67]. Many energy transitions that occur in organics when ultra-violet or visible radiation is absorbed consist of raising these π -electrons from their stable ground states to short-lived excited states. Often, such transitions involve charge transfer within the molecule which normally consists of a region of conjugated electrons substituted with electron donating and/or withdrawing chemical groups (D-A molecules) which are discussed below.

Certain chemical groups, such as $-\text{CN}$, $-\text{NO}_2$ and $-\text{CF}_3$, have the ability to strongly attract electron density from a conjugated π -electron system. Others, such as $-\text{OCH}_3$, $-\text{N}(\text{CH}_3)_2$ and $-\text{O}^-$, can inject electrons into the conjugated region. Both kinds of groups when used together in para-disubstituted ring systems can mutually interact and induce a large electron charge transfer [68] from the donor group towards the acceptor group. The strength with which the various groups inject or withdraw electronic charge can be estimated by considering the Hammett σ -constants (acceptors) and the first ionisation potentials (donor) shown in Table I. Such substitutions have a pronounced effect upon the absorption wavelength of the compound as the ground state and excited state energy levels are perturbed by each group which leads to splitting and narrowing of the energy gap between the highest occupied ground state and the lowest unoccupied excited state. Figure 3.6 shows the effect on the absorption wavelength when a benzene ring is firstly monosubstituted with either a donor or an acceptor group and secondly when it is para-disubstituted with both for the case of para-nitroaniline. It is clear that the energy difference decreases as the "push-pull" effect on the ring increases.

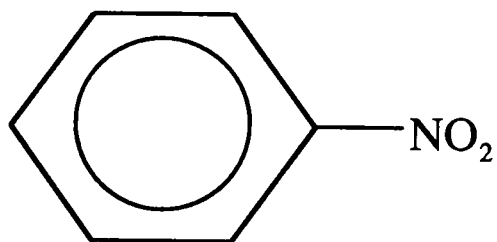
It follows that, in the ground state of D-A molecules, there exists a charge asymmetry, and therefore a dipole moment, along the long axis of the molecule. When the molecule is excited, this dipole moment normally increases owing to the natural tendency of the donor and acceptor groups to push and pull electron density respectively. However, the charge separation that results in response to an applied electric field (in the form of electromagnetic radiation) is linear only until the field becomes very strong. Hence, when using high power sources such as Nd:YAG lasers, the change in induced dipole moment is non-linear with field strength and, as seen previously (equation 3.3), this leads to the generation of harmonic electromagnetic waves. Figure 3.7 shows this property diagrammatically.

TABLE 3.1a : Hammett σ Constants for Several Electron Acceptors.

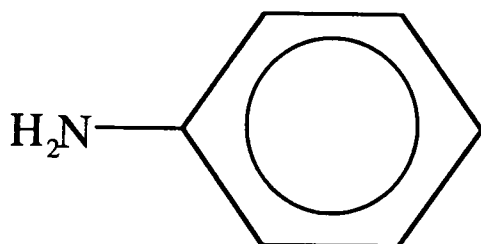
Electron Acceptor	Hammett σ Constant	Effectiveness
H	0.00	
CHO	0.36	
CO ₂ H	0.41	
COMe	0.50	
CN	0.67	
SOClF ₃	0.69	
SO ₂ Me	0.72	
NO ₂	0.78	
SO ₂ CF ₃	0.93	
N ₂ ⁺	1.80	

TABLE 3.1b : First Ionisation Potentials of Several Electron Donors.

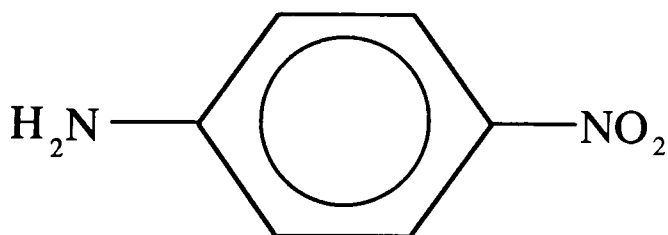
Electron Donor	First Ionisation Potential	Effectiveness
OH	10.8	
OMe	10.0	
SH	9.4	
NH ₂	9.0	
SMe	8.7	
NHMe	8.2	
NMe ₂	7.9	



$$\lambda_{\text{max}} = 269 \text{ nm}$$



$$\lambda_{\text{max}} = 280 \text{ nm}$$



$$\lambda_{\text{max}} = 381 \text{ nm}$$

Figure 3.6 : The effect on maximum absorption wavelength of donor and acceptor substitution.

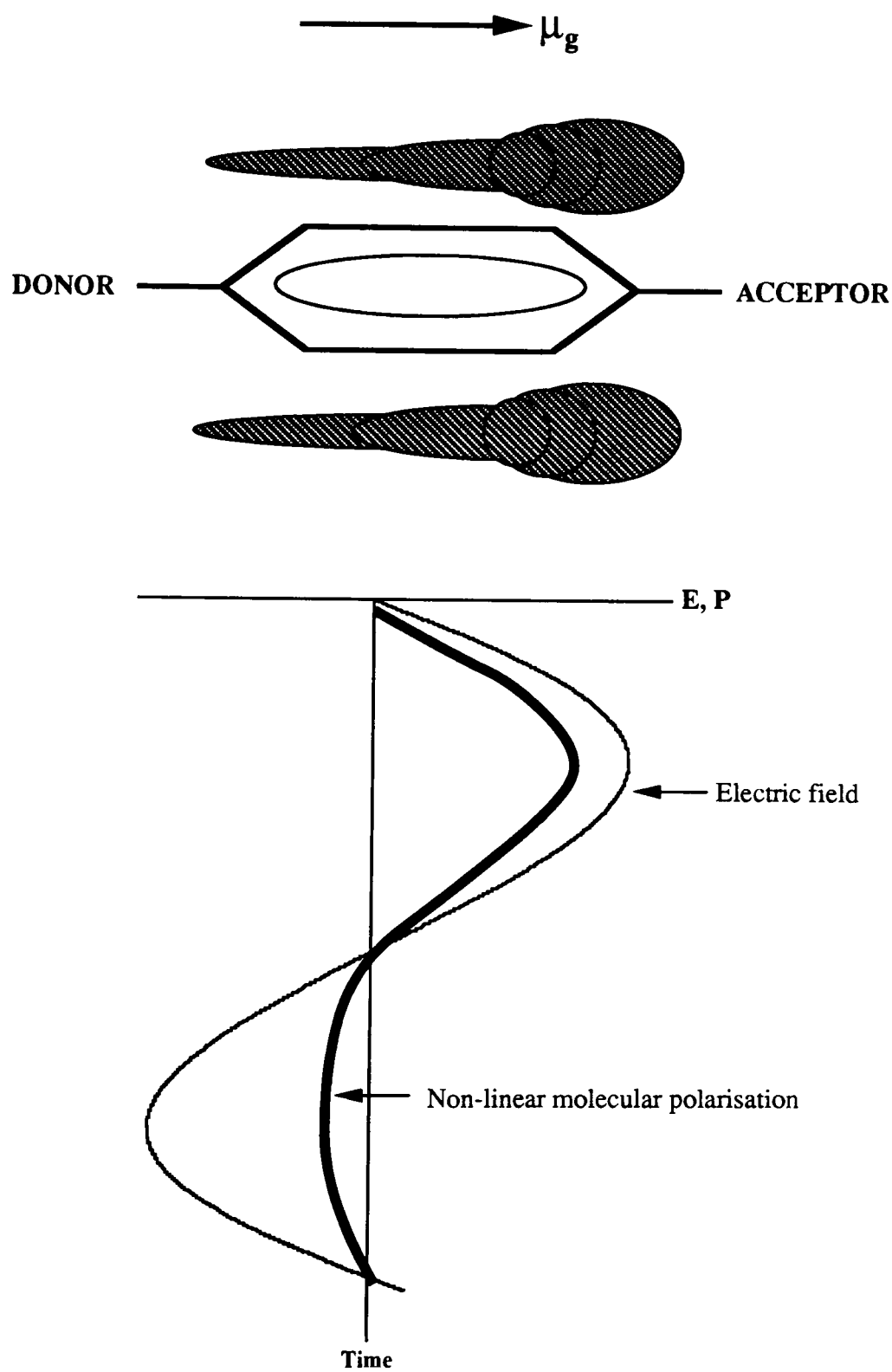


Figure 3.7 : Asymmetric molecular polarisation response to an applied electric field.

The magnitude of the second-order molecular response has been modelled by Oudar [69] who suggested that the second-order hyperpolarisability, β , is made up of two contributions:

$$\beta = \beta_{add} + \beta_{CT} \quad (3.7)$$

where β_{add} = an additive hyperpolarisability term produced by the individual affects of monosubstituting each group, and β_{CT} = the charge transfer component of hyperpolarisability which arises due to the strong mutual interaction of the donor and acceptor groups. Oudar's experiments indicated that β_{CT} was by far the predominating effect. Using quantum mechanical perturbation theory he modelled this contribution as:

$$\beta_{CT} = \frac{3e^2\hbar^2}{2m} \frac{W f \Delta\mu}{[W^2 - (2\hbar\omega)^2][W^2 - (\hbar\omega)^2]} \quad (3.8)$$

in which W = the transition energy associated with the absorption, f = the oscillator strength of the transition, $\Delta\mu$ = the absolute difference in dipole moments of the ground and excited states, and $\hbar\omega$ and $2\hbar\omega$ = the photon energies of the fundamental and second-harmonic radiation.

This expression has far-reaching consequences for the optimisation of organic molecules for second-order optics. Firstly, β_{CT} is directly proportional to the absolute change in dipole moment between ground and excited molecular states. Usually, molecules possessing large ground state moments exhibit extremely large excited state dipoles so that $\Delta\mu$ is large. The most important feature of this relation, however, is that the value of β_{CT} may be dramatically enhanced if the absorption edge of the molecule is tuned to coincide with the photon energy of either the fundamental or the second-harmonic radiation. In the case of absorption near the second-harmonic wavelength, the term (W^2

$(2h\omega)^2$) becomes very small so increasing the magnitude of β_{CT} . This enhancement property is shown schematically in Figure 3.8. However, at this point, it must be noted that although β_{CT} can be very large, the molecules will partially absorb the second-harmonic radiation that is generated. Ideally, therefore, a material is required which absorbs near to the second-harmonic wavelength but does not coincide exactly with it. This transparency - efficiency trade-off is most applicable to single crystal growers who are dealing with thicknesses of typically 5 mm. Thin LB films, however, do not suffer from self-absorption so critically and are thus of great potential use in non-linear integrated optics technology.

(ii) Crystal Structure Considerations.

The quest to find efficient organic non-linear crystals is in fact the search for a polar crystal in which the macroscopic properties reflect the internal asymmetric molecular characteristics. In addition to the ideal molecular properties required for high hyperpolarisability, there is an optimum packing arrangement of the molecules within a crystalline lattice. However, anti-parallel dipole-dipole interactions are highest for large ground state dipole moments and therefore many potentially useful materials tend to adopt centrosymmetric crystal structures which are of no use for second-order applications. Only 10 out of the possible 32 crystallographic point groups in which organics can crystallise are suitable for such effects. This produces a severe restriction on the number of organics that are likely to display a useful $\chi^{(2)}$. In addition, the crystal must be grown to a high degree of perfection and ideally be angle phase-matchable.

Several organics do exist whose $\chi^{(2)}$ values are sufficiently large to be commercially usable such as N-4-nitrophenyl-(L)-prolinol (NPP) [70]. However, it has been shown by Shigorin and Shipulo [71] that only 38% of the molecular non-linearity can ever contribute to the macroscopic susceptibility due to relatively poor packing

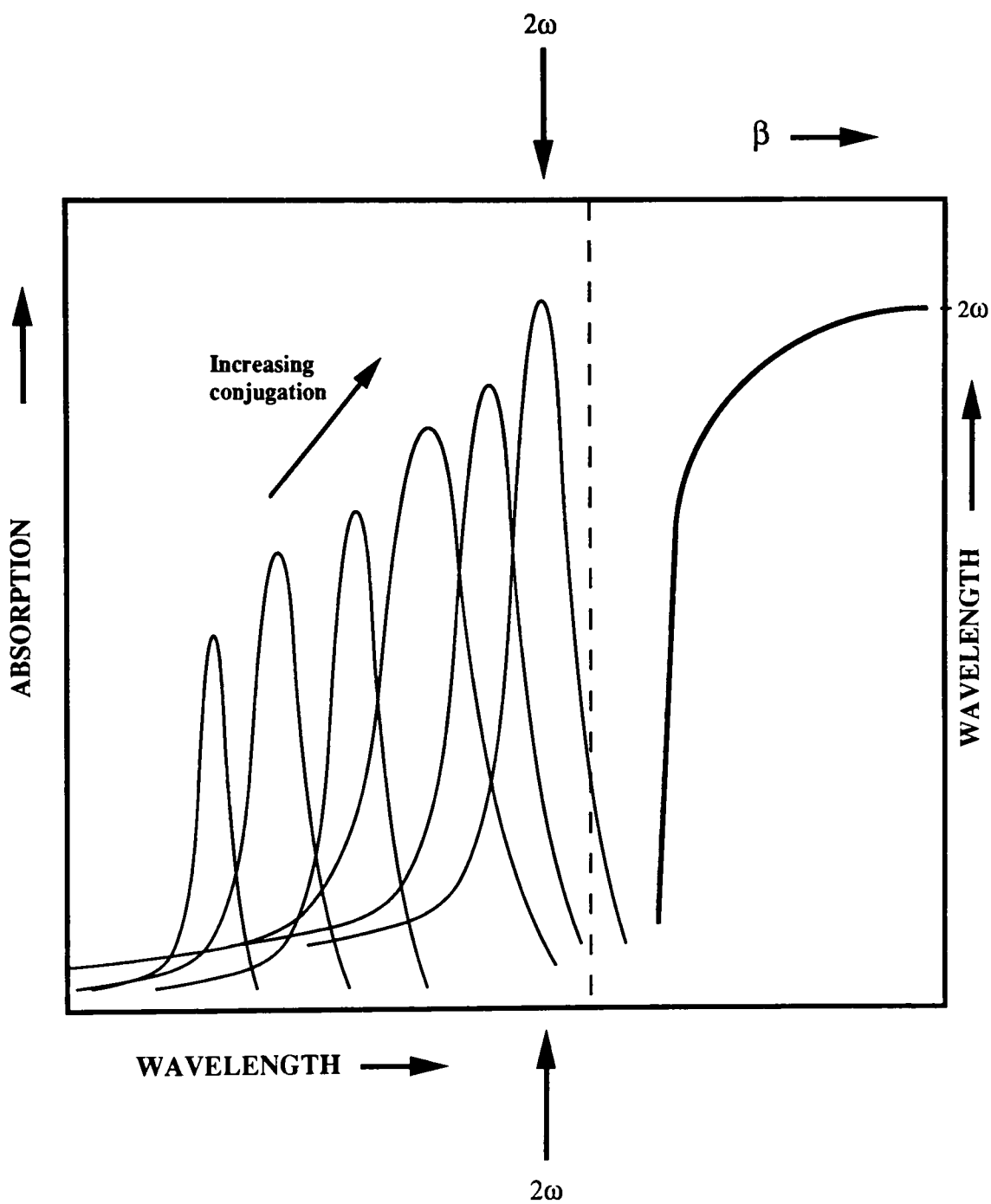


Figure 3.8 : Resonant enhancement of the hyperpolarisability as the absorption wavelength approaches the second-harmonic position.

efficiencies. This problem is overcome with the LB technique in which highly ordered, dipolar arrays of molecules are deposited with high packing densities.

(iii) Other Material Requirements.

Consideration must also be given to other material characteristics such as chemical stability, photostability, laser damage threshold and compatibility with the particular deposition or growth technology in use. To this end, some of the work in this thesis has been involved with the optimisation of the thermal stability of a range of organo-ruthenium complexes in order to improve their tolerance to high power laser sources and to open up a wider sphere of potential applications.

3.2.6 Applications of Non-linear Optical Effects.

The non-linear optical processes described in the preceding sections give rise to many potential applications [72] which are summarised in Table 3.2. Most of the work on new non-linear materials in the solid phase has dealt with bulk single crystals coupled to high power lasers. However, in order to bridge the gap from mere observation of non-linear effects to their actual realisation in practical devices, it is necessary to seek fully optimised non-linear structures. It is a major advantage if the non-linear material may be processed in thin film form as it is then compatible with integrated optics waveguiding technology.

Optical second-harmonic generation is useful in extending the range of usable laser wavelengths. In years to come, high power diode lasers should be available at visible wavelengths (500 - 700nm) which will enable relatively high power ultra-violet laser outputs to be obtained. Such laser wavelengths would open up new avenues in the field of

Table 3.2 : Passive non-linear optical applications.

ORDER	PHENOMENON	APPLICATION
$\chi^{(1)}$	Linear dispersion Refraction	Optical fibres Waveguides
$\chi^{(2)}$	Optical rectification $\omega_1 - \omega_1 = 0$	Hybrid bistable devices
	Electro-optic effect $\omega_1 + 0 = \omega_1$	Modulators Variable phase retarders
	Frequency doubling $\omega_1 + \omega_1 = \omega_2 = 2\omega_1$	Second harmonic generation
	Frequency mixing $\omega_1 \pm \omega_2 = \omega_3$	Optical mixers
	Parametric amplification $\omega_3 = \omega_1 + \omega_2$	Parametric oscillators
$\chi^{(3)}$	Frequency tripling $\omega_1 + \omega_1 + \omega_1 = 3\omega_1$	Deep u.v. conversion
	Intensity-dependent refractive index	-
	Four wave mixing	Phase conjugation Bistability

data storage as an enormous number of uv-absorbing organic molecules would be potentially useful.

The amplitude modulation of a light beam is also achievable using second-order non-linear materials [73]. A large transverse electric field modifies the relative permittivity of such a material. The polarisation of an incoming laser beam can be shifted by an electric field so that, with a suitable arrangement of polarisers, the output intensity of the fundamental beam can be controlled by an applied voltage (Figure 3.9,10). Thus, modulation of a light beam is possible which has obvious uses in the telecommunications industry.

Novel sensors based on $\chi^{(2)}$ optics can be foreseen in which the second-harmonic output power can vary as a function of an external stimulus which is applied to the active layer. For example, the adsorption of gas by a non-linear substance may drastically affect the molecular hyperpolarisability which, in turn, affects the macroscopic behaviour and the performance of the device. Such materials could be coated onto planar waveguides or form the cladding layers of optical fibres allowing remote sensing with no problematic electrical interference.

Third-order materials also have extensive potential applications including optical bistability and phase conjugation. However, the molecular characteristics required for large macroscopic $\chi^{(3)}$ effects are less well-researched and understood than those for second-order phenomena and so it is unclear whether the performance of such materials may be improved greatly from their present level of operation.

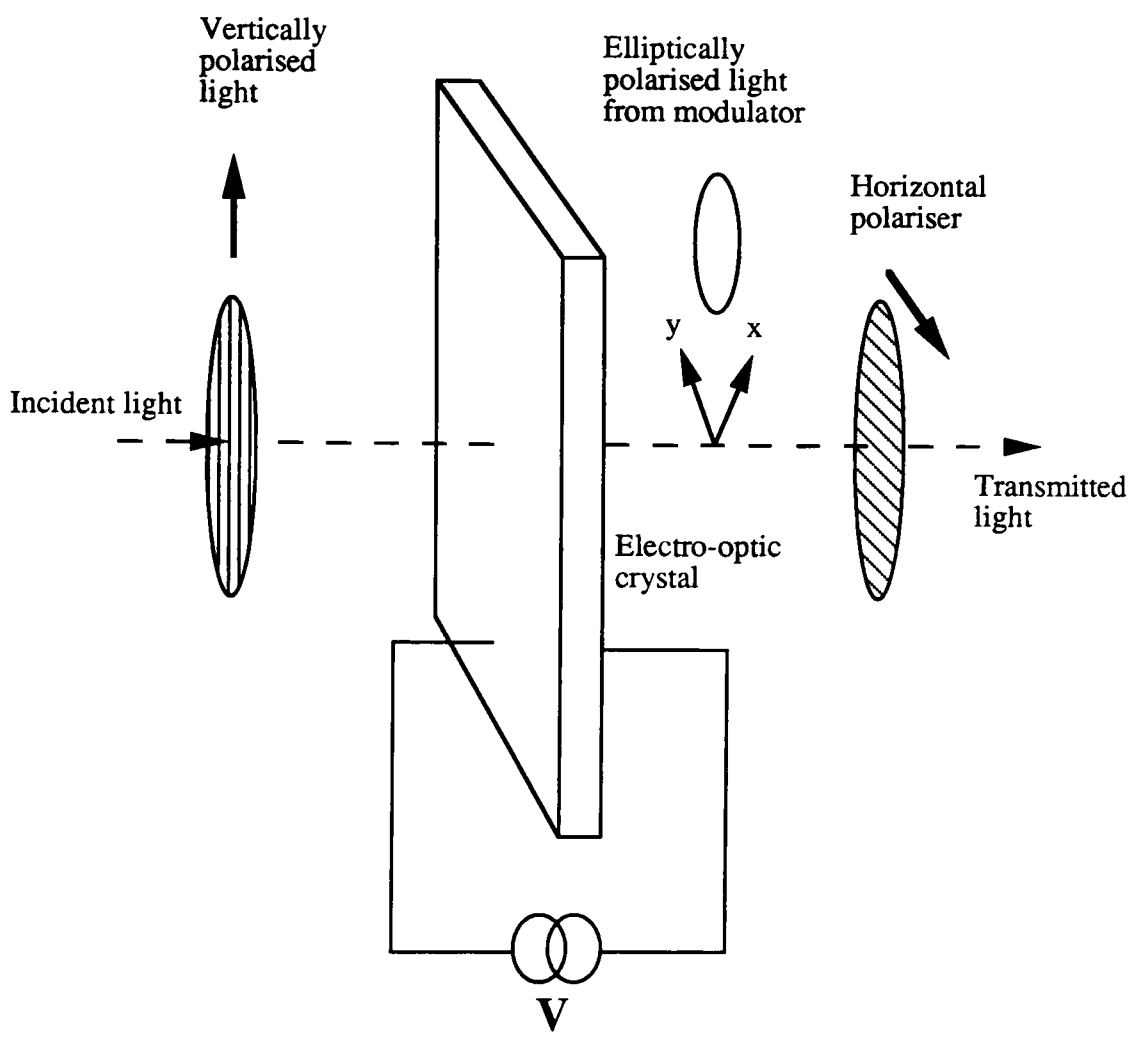


Figure 3.9 : Arrangement of the components of a Pockels electro-optic modulator.

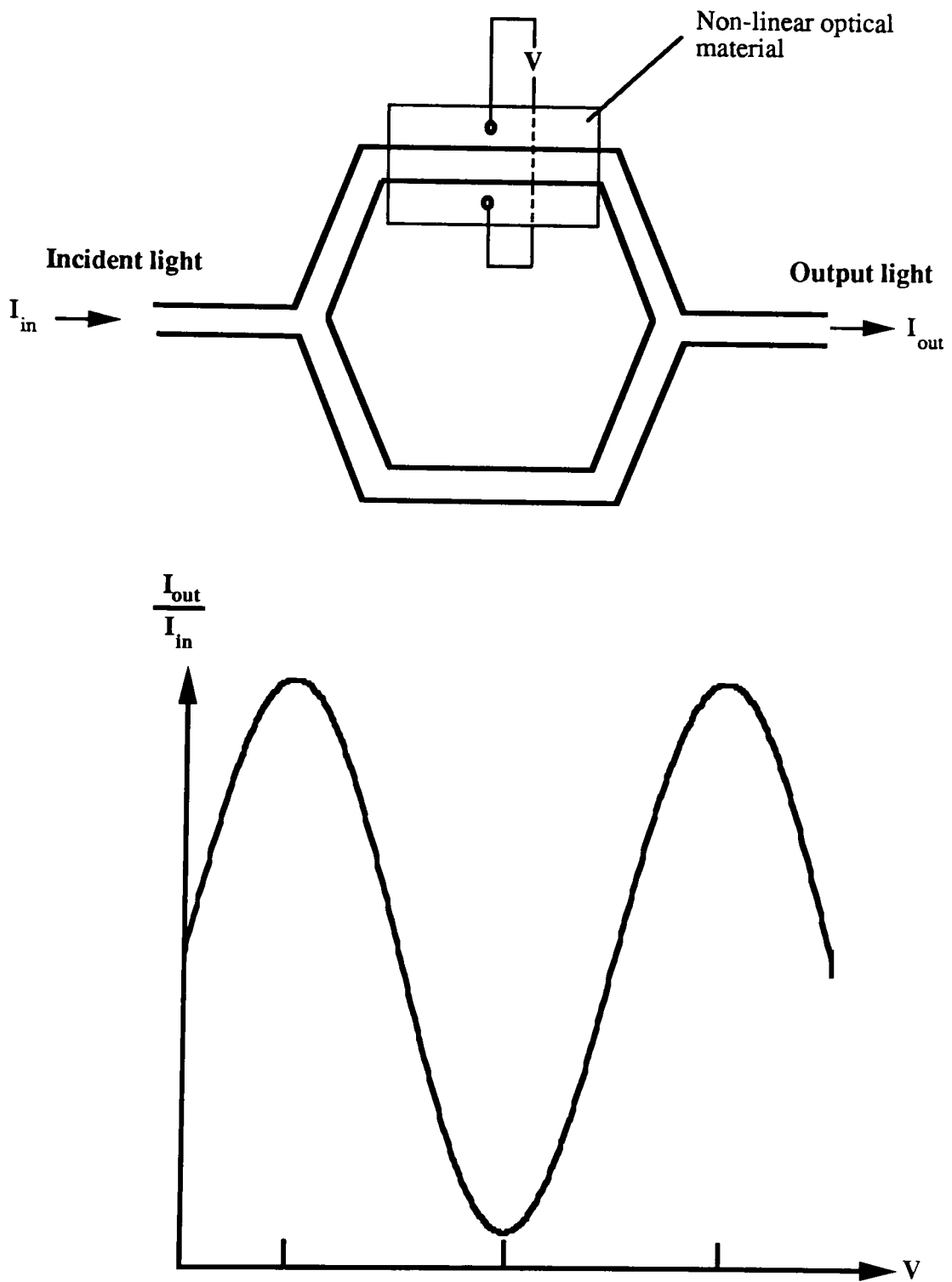


Figure 3.10 : Electro-optic modulation using a Mach-Zehnder type arrangement.

3.3 Pyroelectricity of Organic Compounds.

Many of the organo-ruthenium complexes discussed in this thesis have been shown to exhibit pyroelectricity [74]. Indeed, such is their interest that the investigation has merited another postgraduate research project in its own right. Pyroelectricity has been defined as the existence of a temperature-dependent spontaneous polarisation within a material. Therefore, the appearance of a short-circuit current in the experimental arrangement shown in Figure 3.11 occurs only when a change in the temperature occurs. Only a short description of the subject is given here in order to show how the technique may be used to verify the existence of an asymmetric non-linear structure within an organic LB multilayer.

3.3.1 Physical Origins of Pyroelectricity.

In order to observe pyroelectricity, the individual molecules must possess a relatively large dipole moment and be arranged in an ordered, non-centrosymmetric array in order to take full advantage of the molecular non-linearity. The molecular features required for pyroelectricity are similar to second-order non-linear optics. That is, the substitution of donor and acceptor groups at opposite ends of a highly conjugated electron system lead to a large ground state dipole moment. The mechanisms by which this dipole moment changes with temperature are not fully understood and depend upon the particular material encountered. It has been suggested that the two major possible contributions arise because of ionic interactions or molecular tilting in which the entire molecule tilts thus altering the measured component of the dipole moment normal to the substrate. The normal measurement procedure is discussed in Chapter 4, but briefly, the short-circuit current flowing in the arrangement shown in Figure 3.11, can be expressed as:

$$i_p = p A \frac{dT}{dt} \quad (3.9)$$

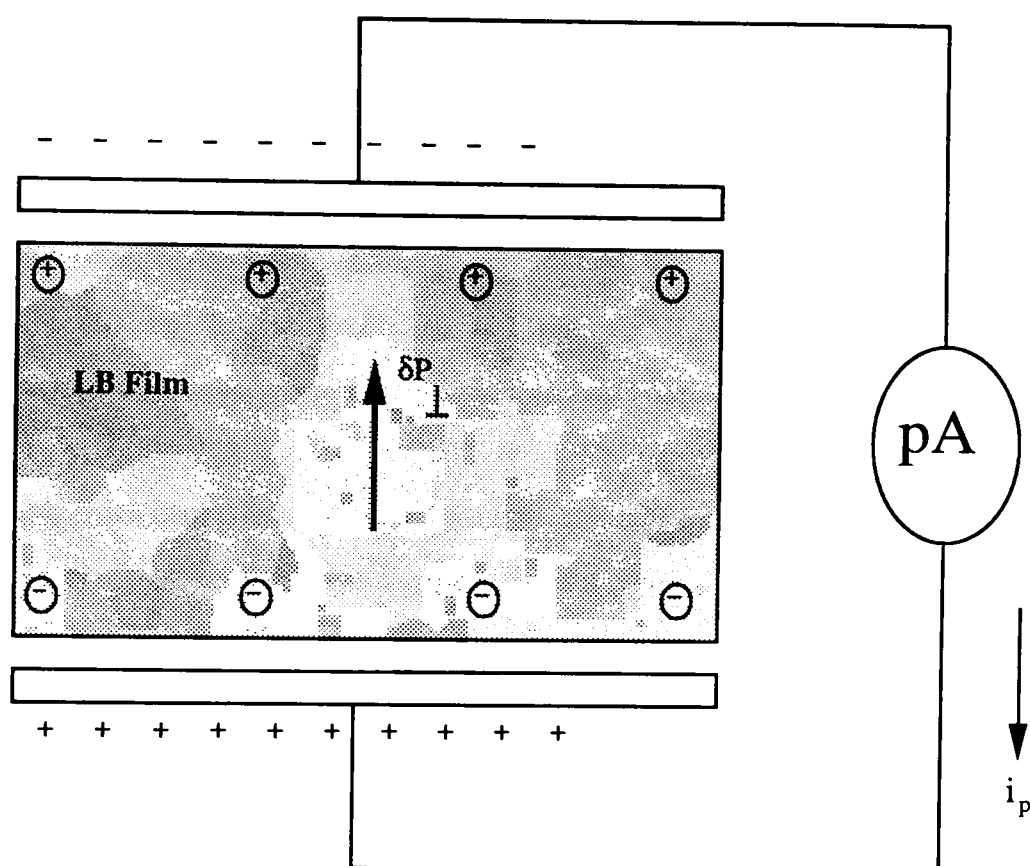


Figure 3.11 : The polarisation change as the temperature is altered in a pyroelectric LB film.

where i_p = the short-circuit pyroelectric current, p = the pyroelectric coefficient, A = the electrode area and dT/dt = the rate of change of temperature. The pyroelectric material forms the insulating dielectric of a capacitor structure. The coefficient p is thus dependent upon the change in the normal component (relative to the capacitor plates) of the electrical polarisation. Much research is continuing at Oxford to elucidate the detailed processes by which this polarisation changes for several classes of organic compounds including the ruthenium complexes extensively characterised in this work. It should be noted, however, that although the pyroelectric coefficients of LB films of these materials are relatively small when compared to other organic compounds, such as PVdF, their figure of merit, defined as the ratio of pyroelectric coefficient to the relative permittivity p/ϵ_r , is large. This value is more important than merely considering the pyroelectric coefficient alone as it allows for noise sources that could occur in the measurement process. It is believed, therefore, that this class of compounds will be of considerable commercial interest for low-level pyroelectric detection for thermal imaging applications in the very near future. Of relevance to the research of acentric LB film structures, however, the appearance of a pyroelectric current verifies the existence of a non-centrosymmetric arrangement of non-linear molecules and can thus be used as an experimental aid in such studies.

3.4 Summary.

In this chapter, some of the non-linear physical properties of organic molecules have been discussed. In particular, the molecular characteristics required for a large second-order non-linear optical hyperpolarisability have been laid out and the need for non-centrosymmetry has been stressed if advantage of the molecular property is to be conveyed to the macroscopic crystal or thin film. The phenomenon of resonance enhancement of hyperpolarisability has been detailed in order to show how the molecular non-linearity may be dramatically increased at the expense of loss of transparency. This

effect is more important in the growth of large molecular crystals than in LB film research as the thinness of LB structures minimises absorption.

Finally, the pyroelectric behaviour of some organics has been mentioned as the particular class of organo-ruthenium compounds developed and characterised in this study has shown significant pyroelectric activity. In addition, the appearance of a pyroelectric current can yield useful information regarding the dipolar alignment within a multilayer LB film.

CHAPTER 4

Characterisation Techniques.

4.1 Introduction.

In this chapter, the most important experimental techniques that have been used to characterise materials for LB deposition will be discussed. The methods fall broadly into four categories: namely, deposition assessment, electrical properties, optical characterisation and thermal properties, although there is considerable overlap between each classification. These techniques have enabled the characteristics of a wide range of novel organo-ruthenium complexes to be assessed for the first time in solution, bulk powder and LB film form.

4.2 Deposition Assessment.

4.2.1 Deposition Profiles.

The most straightforward method to characterise the transfer of a monolayer onto a solid substrate is to monitor the area occupied by the Langmuir film on the water surface during the deposition procedure using an x-t chart recorder. The change in area can be compared to the physical area coated on the substrate. Coloured dye LB films can easily be seen on a glass substrate but this is more difficult when the peak absorption wavelength

occurs in the ultra-violet region of the spectrum. Often breathing on the film clearly shows the extent to which coverage has taken place, although this is not advisable when further deposition is required or if an electrical or optical measurement is to be taken. In this way, an estimate of the deposition or transfer ratio can be made. An ideal deposition profile for a fatty acid deposited using a single layer Langmuir trough was shown in Figure 2.5 .

4.2.2 Piezoelectric quartz microgravimetric assessment.

A slab of single crystal quartz with electrodes on each side will resonate at an extremely well-defined frequency when placed in a suitable electronic control circuit. The frequency is dependent upon the thickness of the slab and the electrode area. Sauerbrey [75] first suggested that such a device could be used to measure the mass and thickness of material deposited onto its surface during a metal coating process. This is because the resonance frequency can be dramatically modified when the device is mass-loaded, and that, indeed, the frequency change is linearly proportional to the deposited mass. The Sauerbrey relation below shows this proportionality:

$$\Delta f = \frac{2f_0^2 \Delta m}{\rho_q v_q A} \quad (4.1)$$

where Δf = the frequency change caused by the material deposition, f_0 = the initial oscillation frequency, ρ_q = the density of the piezoelectric slab, v_q = the propagation speed of acoustic waves in the quartz, Δm = the change in mass associated with the deposition and A = the electrode area.

The method can be easily applied to the characterisation of the deposition of LB films [76]. Moreover, it may be used as a standard, on-line verification technique to monitor the deposition of successive monolayers during the production of multilayer organic

structures. A photograph of the quartz resonance measurement system is shown in Figure 4.1a . The change in resonant frequency for LB films may be written:

$$\Delta f = \frac{2f_0^2 N \delta\mu}{k_q} \quad (4.2)$$

where N = the number of deposited layers, $\delta\mu$ = the mass per unit area per layer and $k_q = \rho_q v_q$. A plot of Δf versus N should yield a straight line relationship with zero intercept and a gradient equal to $2f_0^2 \delta\mu / k_q$. Practically, the quartz oscillator is inserted into the electronic control circuit shown in Figure 4.1b . The frequency of oscillation is monitored using a Philips PM6654 frequency counter. The LB coated device must be thoroughly dry before measurement and at least 5 minutes should be allowed for the oscillation period to stabilise. A plot for cadmium behenate is shown in Figure 4.2, confirming the reproducibility of the LB deposition process. Care must be taken when comparing values of the gradient for several materials or devices however. There is often a significant variation in the actual surface area of the electrodes due to surface roughness which may lead to the deposition of a slightly different mass per unit area for different devices.

4.2.3 Structural studies.

It is essential to study the structural characteristics of both the floating Langmuir layer [77] and the deposited LB layers [78] in order to obtain information regarding the crystallinity and uniformity of the layers. Several techniques are available which are briefly outlined below.

(a)



(b)

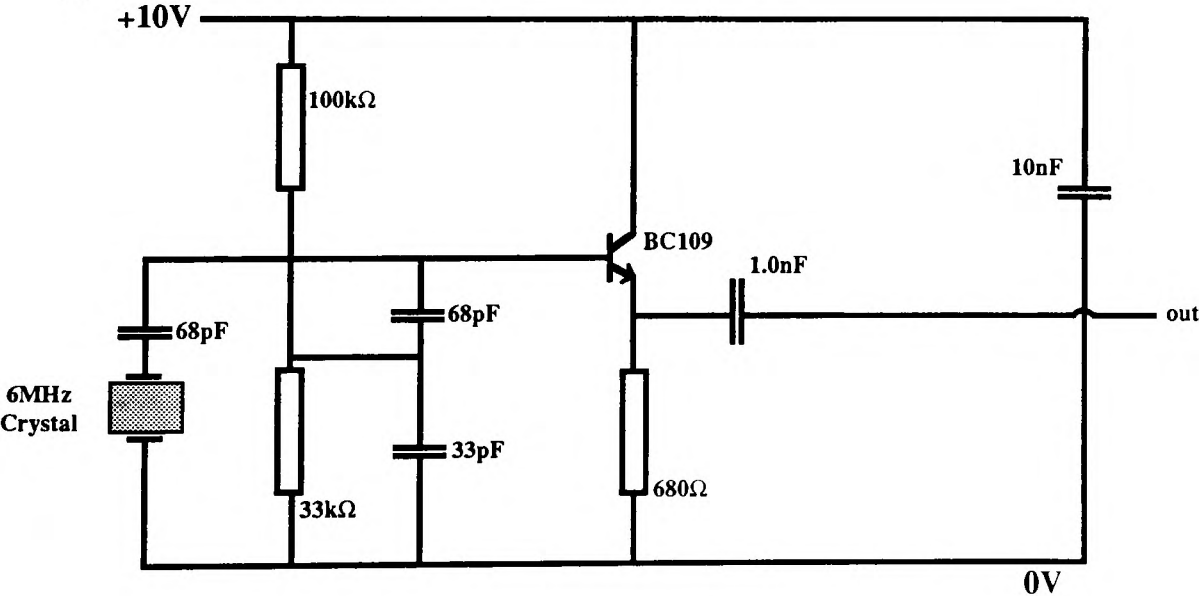


Figure 4.1 (a) The equipment used to observe the change in resonance frequency of a bulk quartz crystal oscillator when it is mass-loaded with LB monolayers. (b) The electronic control circuit into which is placed the bulk oscillator.

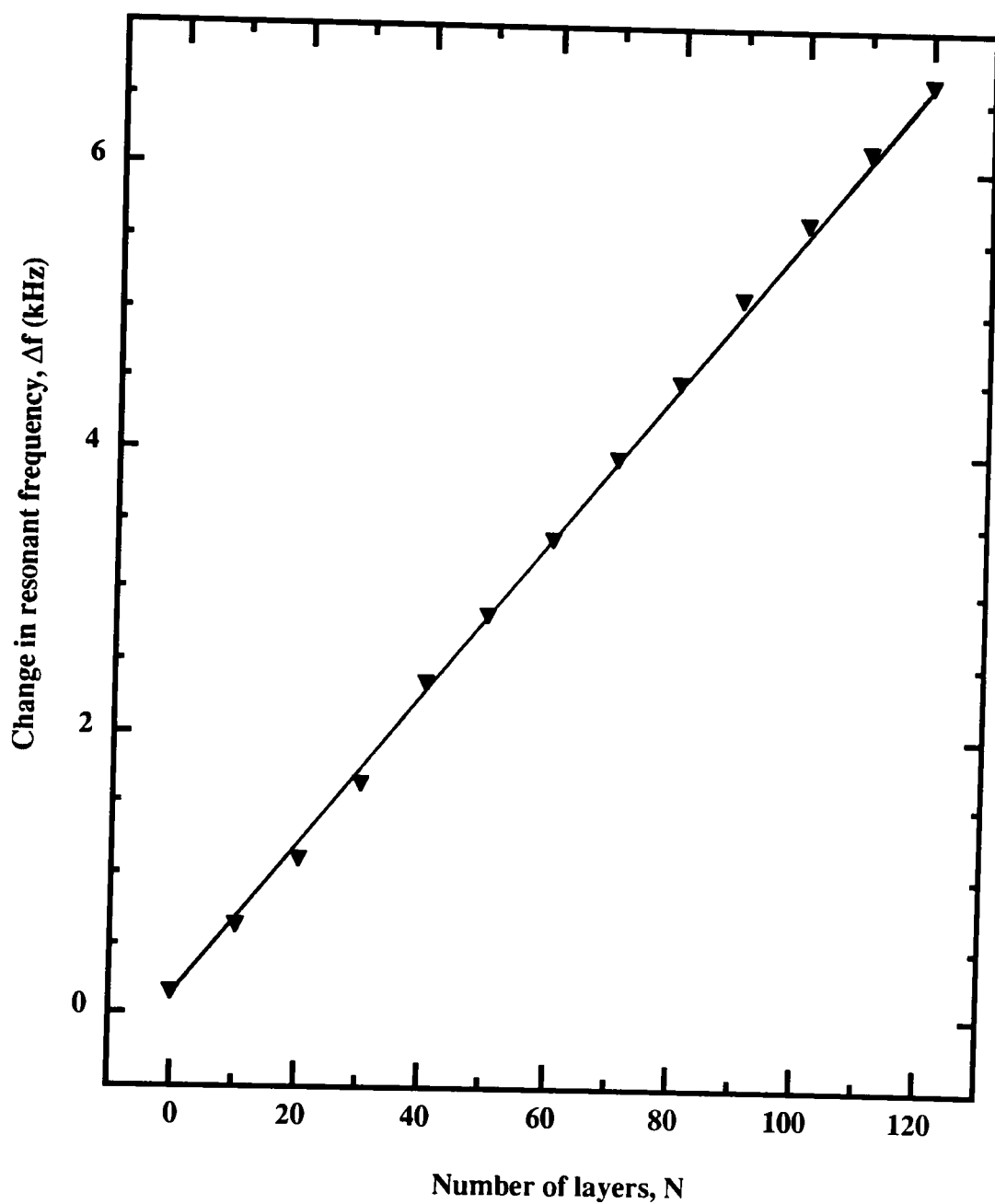


Figure 4.2 : The change in resonant frequency of a 6MHz bulk quartz crystal oscillator when cadmium behenate monolayers are deposited onto its electrodes.

(i) Diffraction techniques.

Information on the structural details of the molecular thin film crystal can be obtained using X-ray, neutron and electron diffraction techniques [79]. Figure 4.3 shows an X-ray diffraction pattern data obtained from 43 layers of pre-deuterated manganese stearate [80]. The precise regularity of the layer spacings lead to well-defined peaks which yield invaluable data about the relative positions of the molecules. Figure 4.4 shows a neutron diffraction pattern from a cadmium arachidate multilayer [81]. Reflection high energy electron diffraction [82] is a rapid and useful technique for structural identification which is not dependent upon highly elaborate sample preparation. The class of molecular packing and the tilt of the molecular chains may be obtained using this technique. Transmission electron diffraction (TED) studies [83] can supplement this data by yielding lattice parameters from even a single monolayer although great care must be taken to minimise the beam damage problems that usually occur with organ materials. This technique has been used in this work to investigate the structure of novel materials.

(ii) Electronic spectroscopy for chemical analysis (ESCA).

This technique [84] provides useful information concerning the elemental composition of the surface of a thin film. Incident X-ray radiation causes the removal of inner-core electrons from the atoms closest to the surface whose energies may be measured and related to particular elements. Thus the energy profile effectively provides a "fingerprint" of the elemental make-up of the structure.

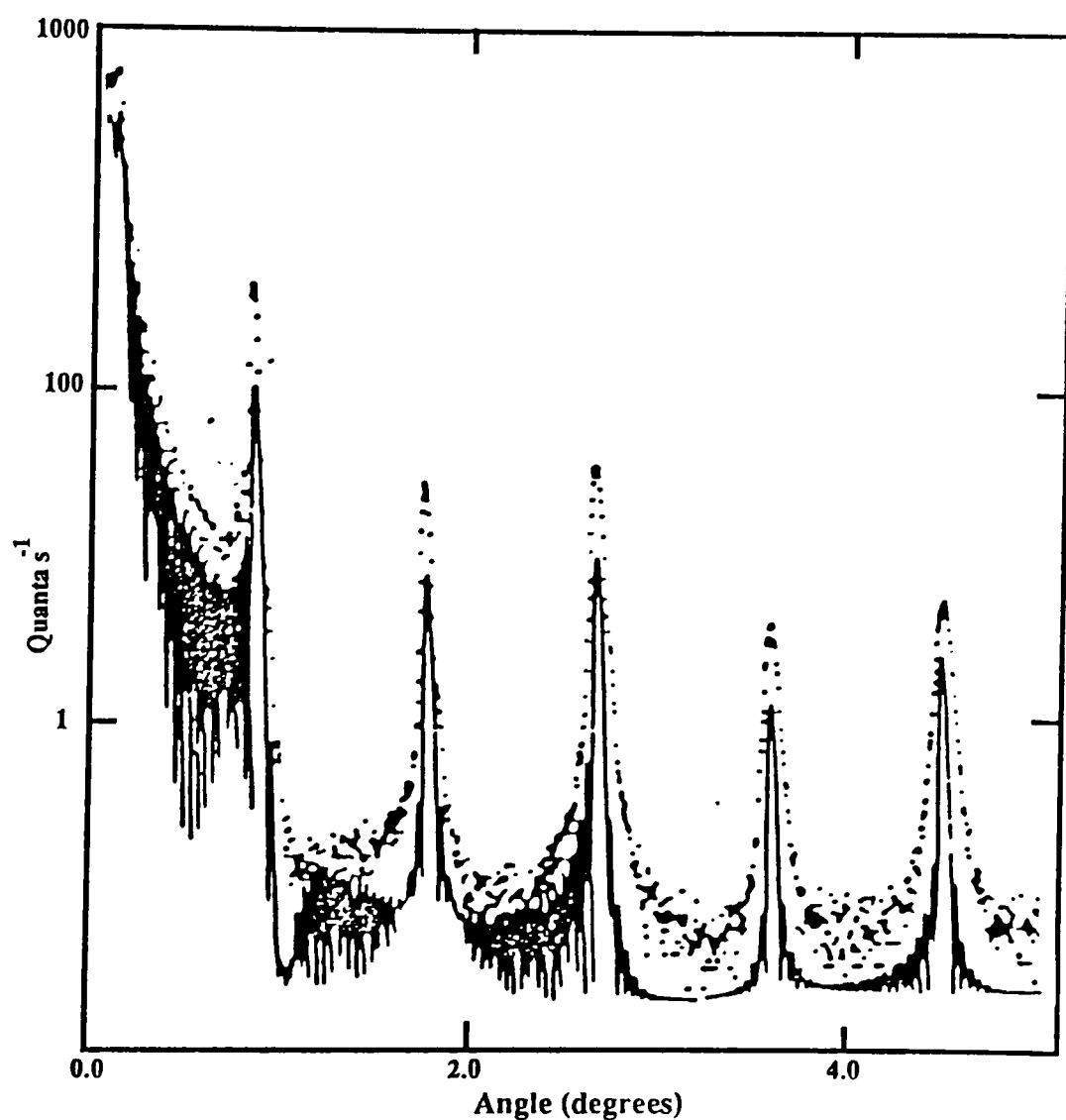
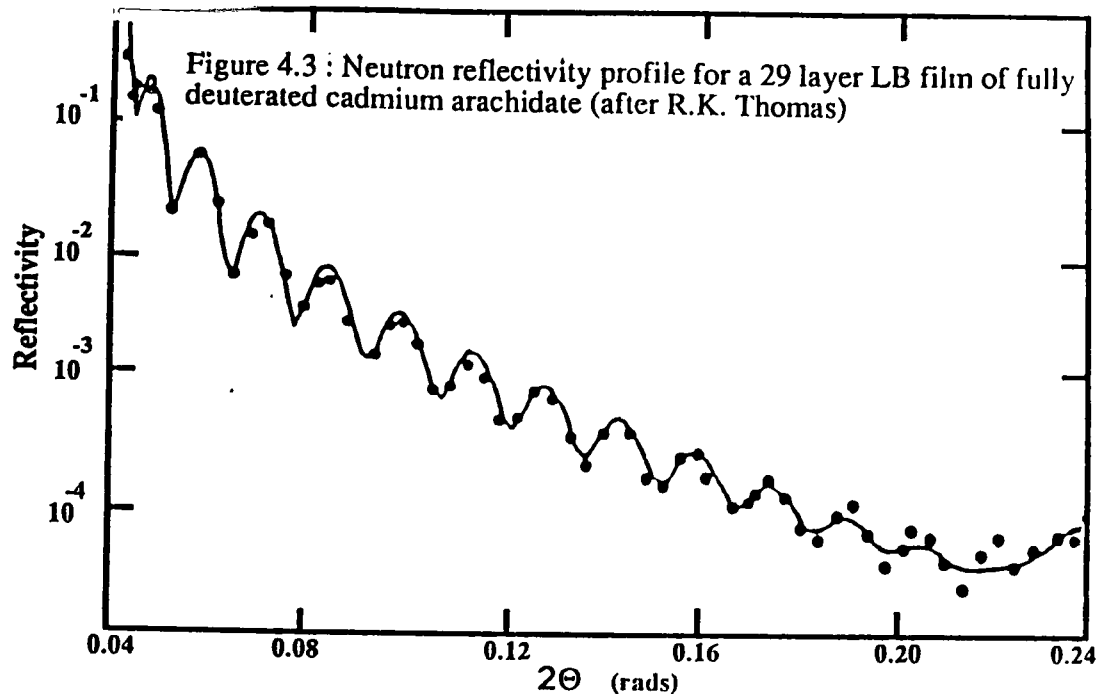


Figure 4.4 : X-ray diffraction pattern from 43 layers of predeuterated manganese stearate (after Nicklow et al).

(iii) Ellipsometry.

Ellipsometry [85] provides useful data regarding the refractive index and thickness of a thin film and is, therefore, of great assistance in verifying the molecular orientation within the LB film. The technique has been used in this work to investigate the thickness of novel organo-metallic LB layers.

(iv) Scanning optical microscopy.

Scanning optical microscopy [86] enables the surface structure of deposited LB films to be observed readily and contrasted to substrate materials in order to establish the quality of the layer. Higher resolution is achievable than in conventional microscopy. It has been used here briefly to examine the contrasting quality of several different molecular films.

4.3 Electrical Characterisation.

4.3.1 Measurement of Dielectric Thickness.

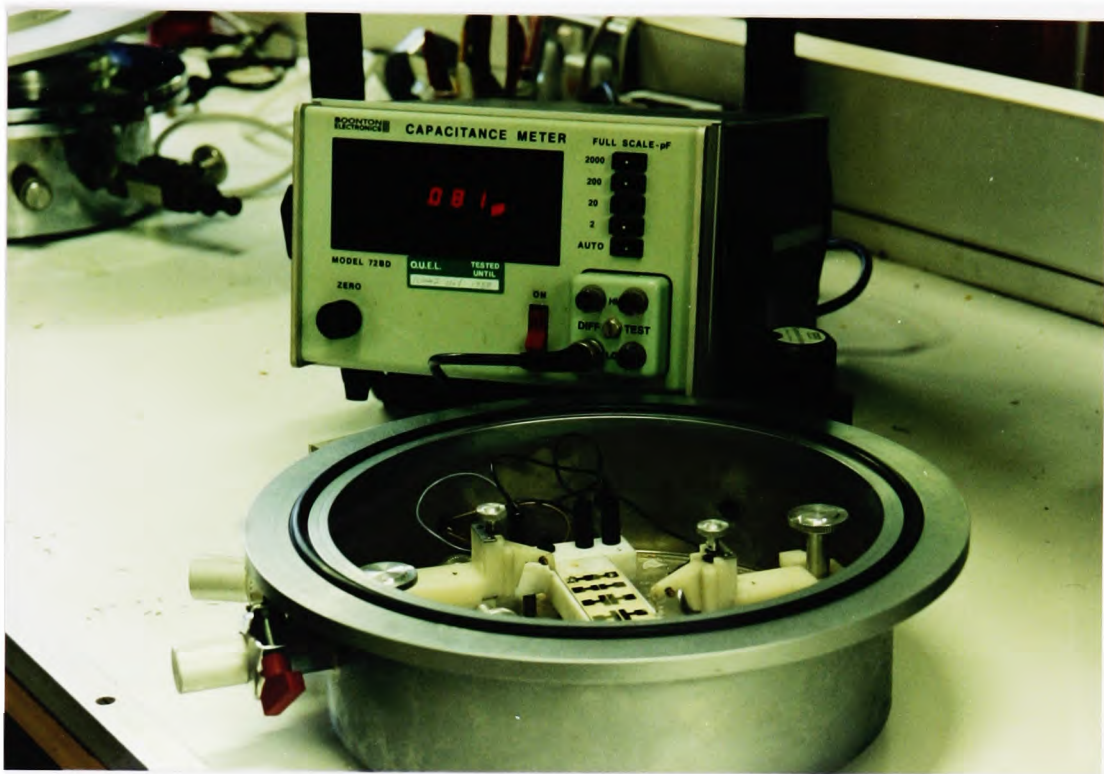
An important method of examining the uniformity of deposition and electrical integrity of an insulating LB film is to measure its dielectric thickness: that is, the relative permittivity [87]. For instance, a region of pin-hole free insulating material will exhibit a well-defined capacitance depending upon its thickness, dielectric constant and the area of the electrodes. When pin-hole defects are present, however, metal filaments often penetrate the insulating layer via the defects during the electrode evaporation process resulting in short-circuiting between electrodes or, at least, severe disruption to the structure of the film. Such damage is exposed by the capacitance measurement. The insulator capacitance, C_i in an metal-insulator-metal (MIM) structure is given by:

$$\frac{1}{C_i} = \frac{d}{A\epsilon_0\epsilon_r} + \frac{1}{C_{ox}} \quad (4.3)$$

where ϵ_0 , ϵ_r = the permittivity of free space and the relative permittivity of the insulator respectively, d = the thickness of the layer. C_{ox} arises from the presence of an oxide layer on the bottom electrode which is usually aluminium. The upper electrode is normally made from gold to simplify the analysis. In an LB film, the total multilayer thickness is equal to $N.d$ where N is the number of monolayers and d is the monolayer thickness. A plot of inverse capacitance as a function of the number of layers should yield a straight line with a positive intercept owing to the metal oxide layer, provided that the reproducibility and uniformity of deposition are high. The gradient exposes the dielectric thickness from which a value of the relative permittivity can be calculated if the monolayer thickness is estimated. A plot for cadmium behenate is shown in Figure 4.5b . The dielectric thickness is equal to 1.2×10^{-9} m, which is consistent with a permittivity of 2.5 for a layer thickness of 3.0 nm.

The capacitance of the MIM structure was measured using a Boonton Electronics Model 72BD capacitance meter (1MHz). A contact is made to the bottom aluminium electrode using a gold wire and conducting silver paint. An array of small, circular gold dots is evaporated onto the LB film using a shadow mask to form the top electrodes and a gold ball pressure contact is made to each dot in order to complete the circuit. Usually, a staircase structure of LB film is constructed so that several film thickness may be assessed on a single substrate thus eliminating problems with variations in oxide thickness. The devices are held in an earthed sample chamber which may be evacuated. The apparatus is shown in Figure 4.5a .

(a)



(b)

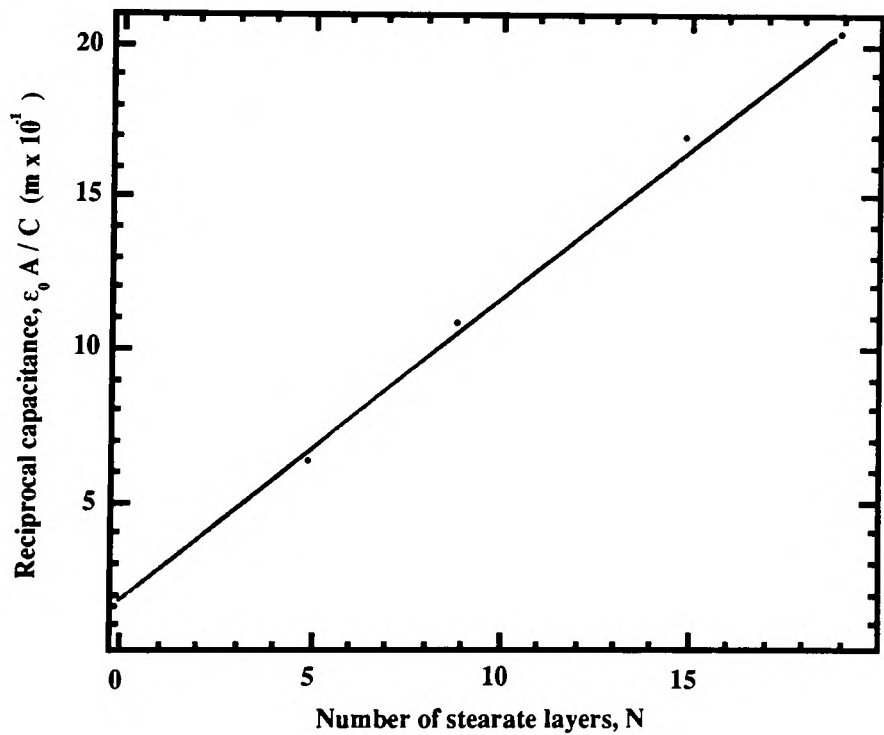


Figure 4.5 : (a) A photograph of the apparatus used to measure the capacitance of metal - LB film - metal structures and (b) a plot of reciprocal capacitance versus number of layers for cadmium stearate.

4.3.2 Electrical conductivity.

The electrical conduction properties of organic films are very complex [88]. Indeed, there are several possible mechanisms by which charge may be transported from site to site. DC current - voltage characteristics for LB layers may be obtained for both lateral conduction and conduction normal to the plane of the substrate. A Keithley 617 electrometer is used to monitor the current which flows in response to a voltage from a Times Electronics calibrated voltage source. The measurements are performed in an evacuated, earthed chamber. Usually, the metal electrodes are palladium or gold to avoid problems with oxide layers whose electrical properties may dominate the conduction through the device. It must be stressed that such measurements are very sensitive to the ambient conditions, so that extreme care must be taken in order to obtain reproducible results.

4.4 Optical Characterisation.

The following section is concerned with the use of optical techniques to characterise novel materials.

4.4.1 Uv-visible spectroscopy.

Electronic transitions occurring in organic compounds may be most commonly excited by electromagnetic radiation in the wavelength range 200 - 1100 nm [89]. The energy of the transitions depends upon the exact composition of the molecule. For instance, compounds that absorb in the visible region of the spectrum are usually highly conjugated and contain electron withdrawing and donating chemical groups such as the bright orange, "push-pull" carotenoids. Conversely, an investigation into the absorption of

electromagnetic radiation by an organic compound can yield useful information concerning its intramolecular and intermolecular properties. In this research, the technique has been used to examine the ultra violet and visible spectroscopic properties of an extensive series of novel organo-ruthenium complexes in solution and thin film form for the first time.

It is often instructive to study the solution spectra of a compound in order to determine the wavelengths of its main electronic transitions and to validate the Beer-Lambert law [90]. This states that the intensity of light emerging from an absorbing medium of thickness δ , absorption coefficient α , and concentration γ will be I_f where:

$$I_f = I_0 \exp(-\alpha\delta\gamma) \quad (4.4)$$

and I_0 = the incident light intensity. However, it is usual to rewrite as:

$$I_f = I_0 10^{(-\epsilon\delta\gamma)} \quad (4.5)$$

where $\epsilon = \alpha / 2.303$ and is the molar absorption coefficient. Therefore:

$$-\log_{10} \left(\frac{I_f}{I_0} \right) = \epsilon\delta\gamma = A \quad (4.6)$$

in which A is defined as the optical density or absorbance. The absorbance is, therefore, directly proportional to the thickness of the sample and the concentration. Figure 4.6 confirms this relationship up to a concentration of 5×10^{-5} moles/litre for a highly absorbing azobenzene compound. An investigation of the relationship between absorbance and solution concentration exposes high concentration effects such as molecular aggregation. Some of the phthalocyanine dyes, for example, dimerise in strong solutions [91] as indicated by the relationship shown in Figure 4.7 in which the dimer absorption peak grows nonlinearly at high concentration. Such intermolecular phenomena are

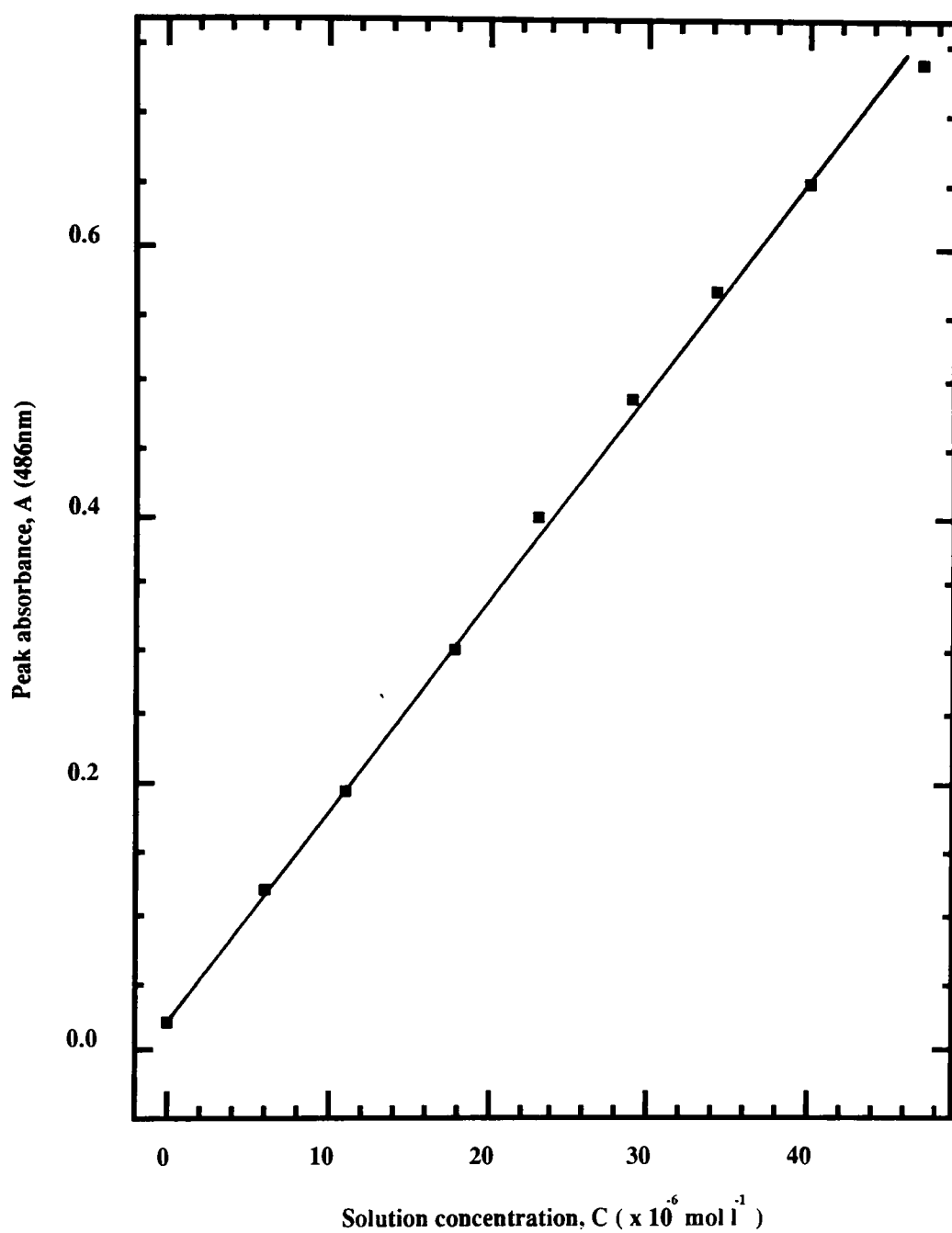


Figure 4.6 : A Beer-Lambert plot for an azobenzene compound showing the linearity of the peak absorbance as a function of solution concentration.

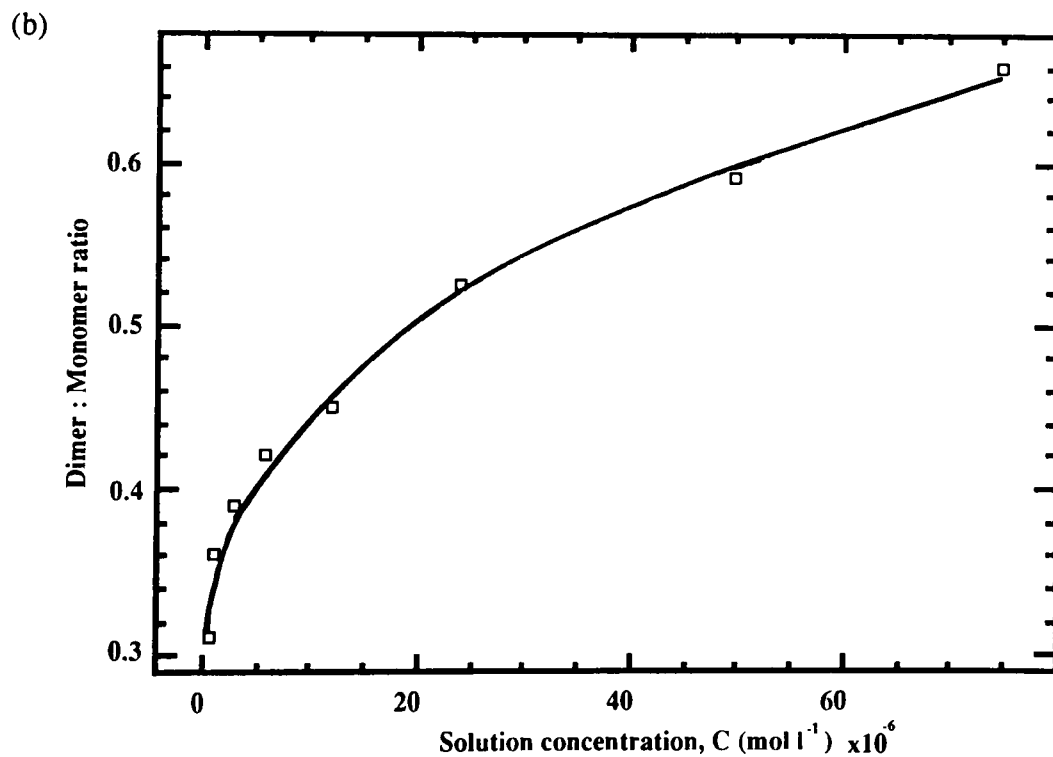
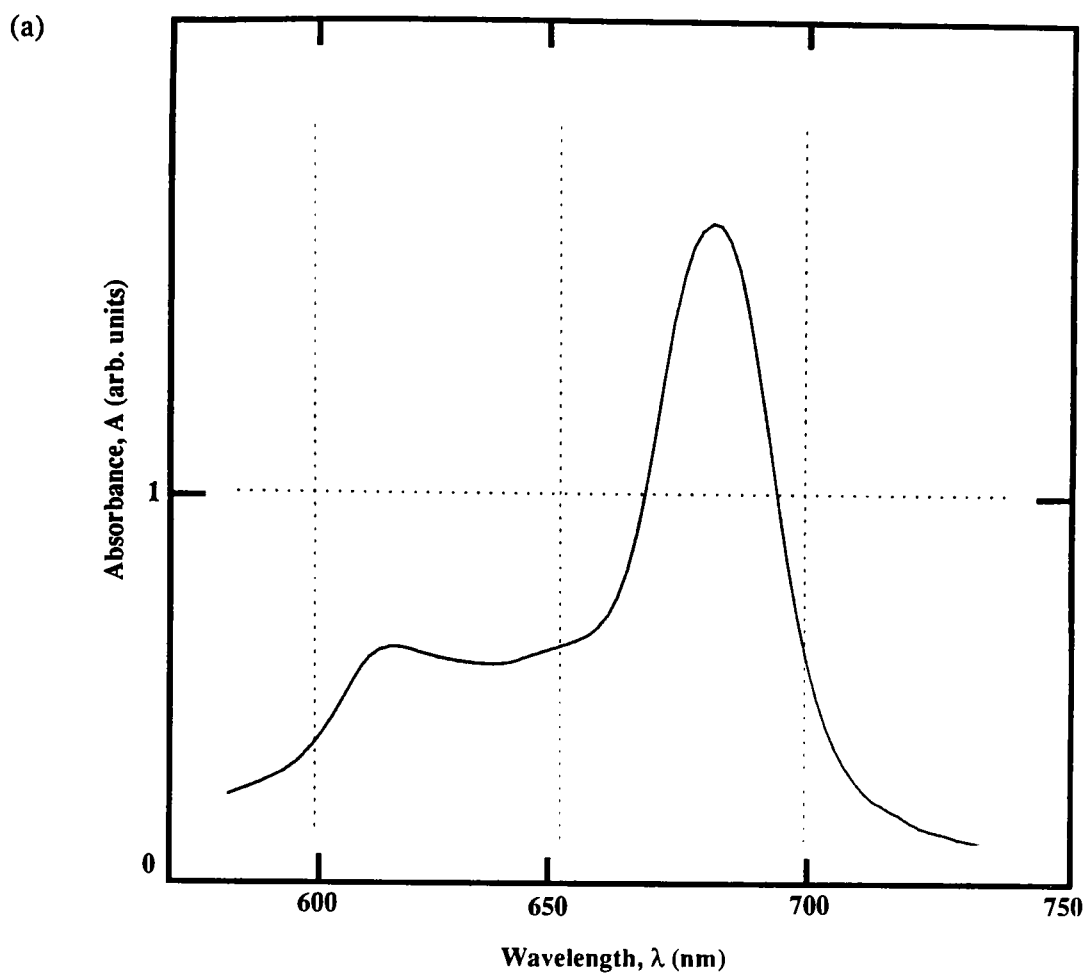


Figure 4.7 : (a) A phthalocyanine absorption spectrum (solution) showing two peaks corresponding to a monomer (632 nm) and a dimer (677 nm) species and (b) the dimer to monomer peak ratio plotted as a function of solution concentration indicating the growth of the dimer population.

important as the molecules will be very densely packed in the Langmuir and LB film. The chemical stability of a compound in a solvent is also significant as the molecules must be spread from a solution onto the water surface. Often a subtle chemical change can be easily detected using absorption spectrometry.

The reproducibility of the LB deposition may be monitored by the measurement of absorption spectra of the transferred, solid films. The concentration term, γ , in the above expressions corresponds to a term $N \cdot d$ where N = the number of transferred layers and d = the monolayer thickness. Thus, the absorbance should scale linearly with the number of layers. Figure 4.8 shows the peak absorbance for LB films of several thicknesses of an azobenzene compound which has been mixed with behenic acid in order to improve the deposition. The linearity of the relation confirms that the reproducibility of monolayer transfer is excellent. However, it is important to note that the reflection of light from thin films is greatly modified when the thickness approaches a quarter wavelength. The apparent absorbance is also affected and, therefore, this must be considered when analysing data. For visible radiation of 600nm, for example, the anti-reflection condition occurs and corresponds typically to 40 - 60 monolayers. In this work, thicknesses up to 20 layers have been studied using this technique. The quartz resonator method was chosen for characterising thicker multilayer structures in order to circumvent the problem mentioned above.

It is also possible to obtain spectra from the floating Langmuir film. Such data can yield useful information concerning the orientation, re-ordering and dissolution of the molecules within the monolayer.

The apparatus used to record the absorption spectra is an Otsuka Electronics MCPD - 100 311C Spectrophotometer which is shown in Figure 4.9 . Two light sources may be used such that the total range of available wavelengths is 267 - 1254 nm . The light is

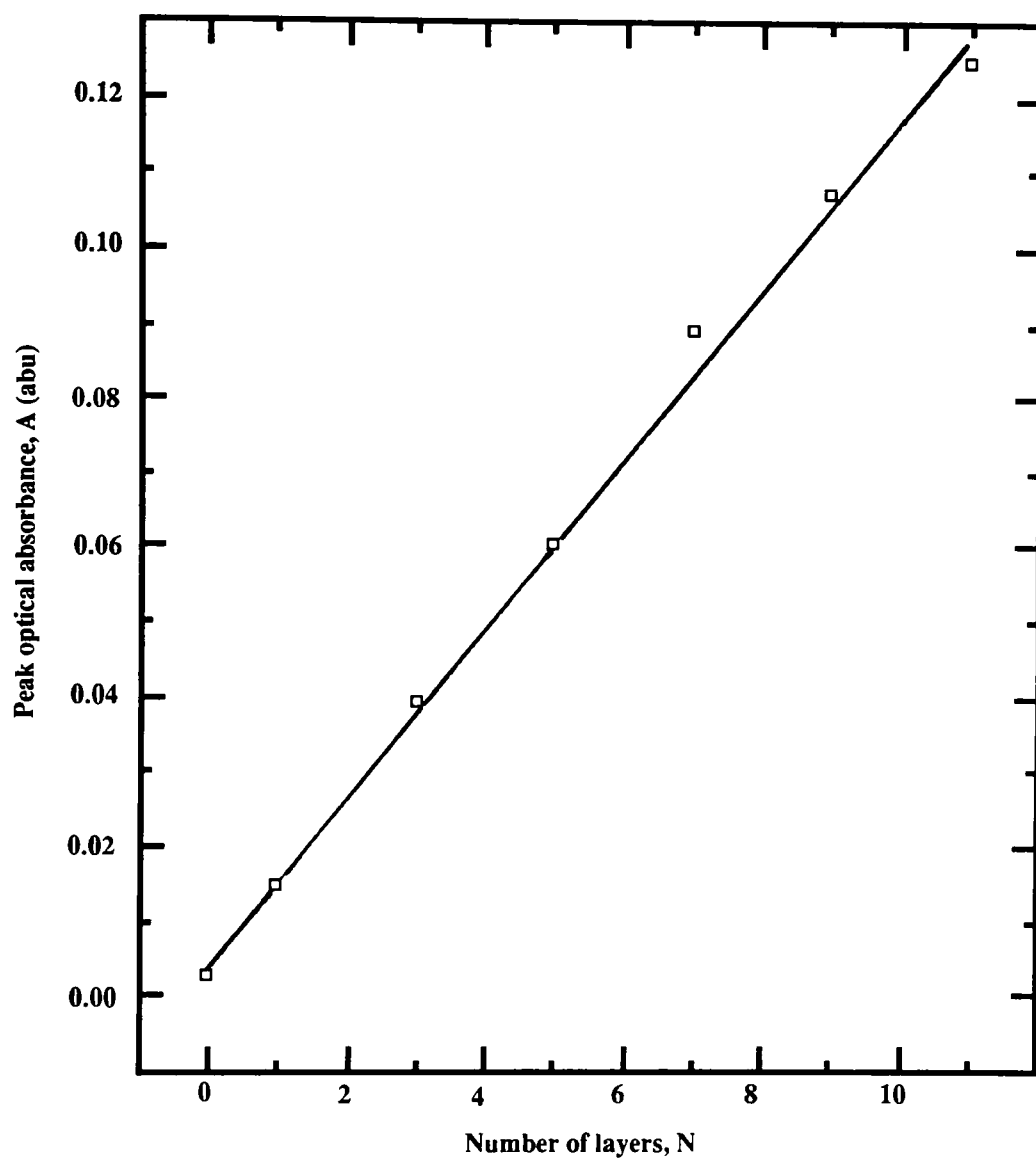


Figure 4.8 : The peak absorbance versus number of layers plot for a mixed behenic acid and azobenzene LB film showing the reproducibility of the successive transfer of monolayers.

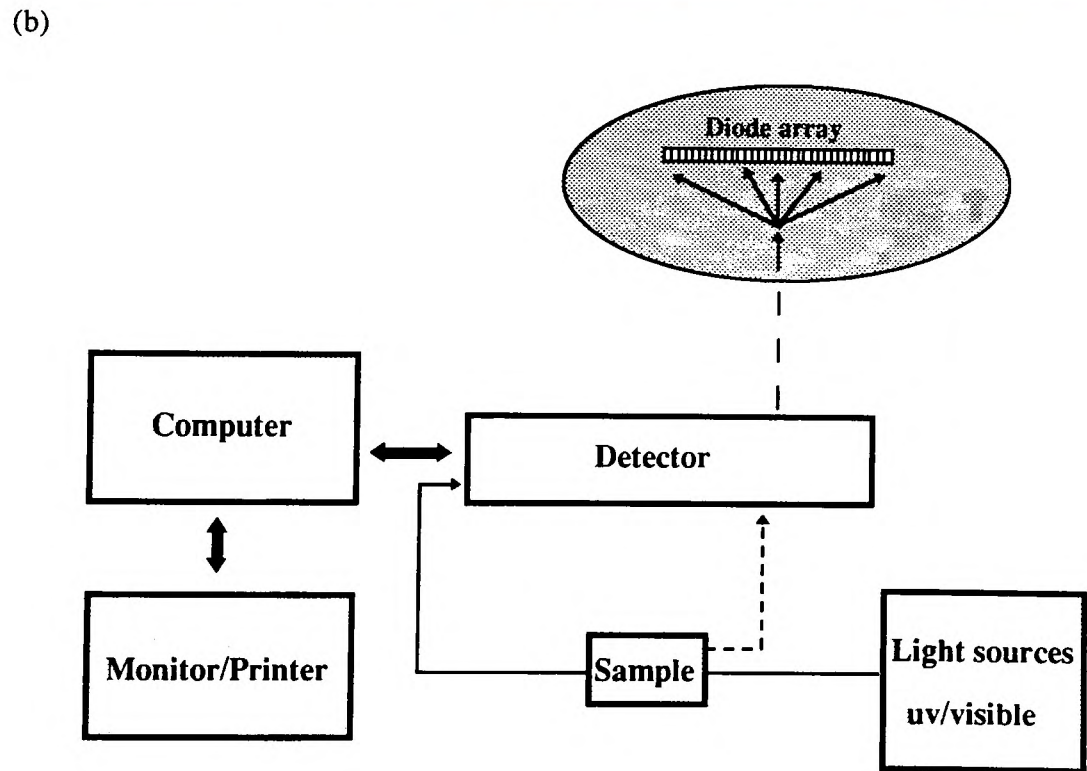
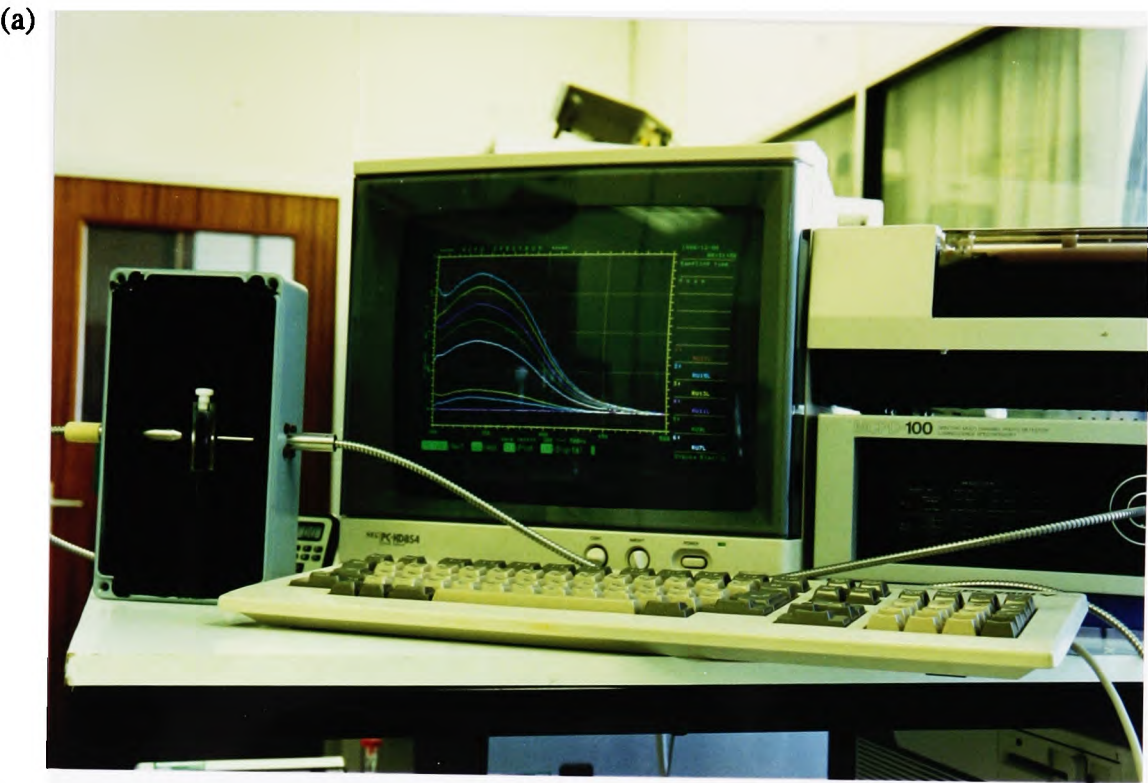


Figure 4.9 : (a) A photograph of the MCPD-100 311C spectrophotometer used to measure the spectral characteristics of the materials studied in this work and (b) a schematic diagram of the spectro-photometer.

carried and collected to and from the sample by means of optical fibres. This offers a distinct advantage over more conventional instruments in which the sample must be confined within a fixed chamber. The collected light is split into its composite spectrum by a diffraction grating and falls onto a 512 component photodiode array. This arrangement enables the entire spectrum to be recorded in a very short period of time: as little as 12 ms for the visible range compared to several minutes for standard equipment offering the same spectral resolution. The high speed of operation allows spectral changes, caused by photo-oxidation processes, dissolution or aggregation, for example, to be monitored as a function of time and can therefore expose interesting properties regarding the chemical stability of the material in solution, Langmuir layer and the LB film.

The spectra are all stored in the central controlling computer and may be manipulated so that their most interesting features can be observed in detail. Both transmission and reflection geometries can be used, which coupled to the large wavelength range, makes the instrument an extremely versatile research tool.

4.4.2 Electric field induced second harmonic generation.

The second order non-linear optical properties of organic compounds may be assessed using a variety of techniques which have been mentioned in Chapter 2. It was stressed that the most vital criteria that a material must satisfy in order to exhibit a second order non-linear optical response are that the molecules themselves must be highly polar and the macroscopic structure must be noncentrosymmetric. Often, organics crystallise with a centre of symmetry so that an attempt to measure the non-linear properties of the solid may not yield any information regarding the inherent molecular non-linearity even though this may be large. A technique is required, therefore, which exposes the second

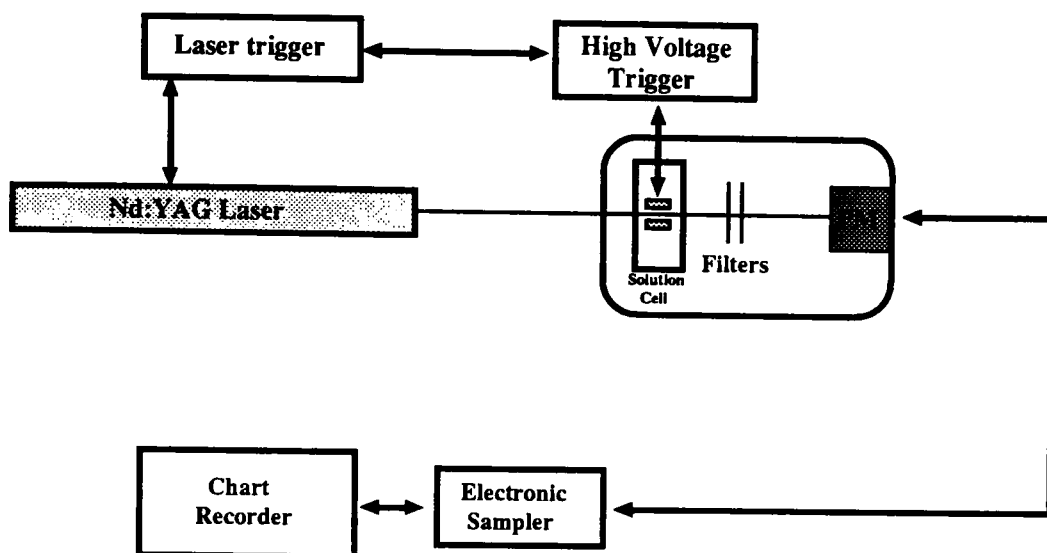
order molecular non-linearity, or the molecular hyperpolarisability, as it is known. Such a method is electric field induced second harmonic generation (EFISHG) [92].

The statistical alignment of polar molecules in solution may be implemented by the application of a large dc electric field. If the field is synchronised to the trigger pulse of a high power laser, then, provided its polarisation is chosen correctly, the optical field may be co-directional with the applied electric field across the solution. Optical frequency doubling can then be observed if the molecules are themselves asymmetric.

It is important to characterise the non-linear optical behaviour of the material in solution form as this measurement verifies the existence of a large non-linearity within the discrete molecule. The researcher may then use a variety of processes, such as crystal growth, polymer spinning or LB deposition, in order to attempt to take advantage of the inherent molecular property and so produce a macroscopically non-linear structure. In particular, the LB deposition process itself enables the required bulk asymmetry to be achieved in the solid phase. A knowledge of the properties of the free molecule obtained using EFISHG distinguishes those compounds which merit further investigation in thin film form.

Figure 4.10a shows a schematic diagram of the experimental arrangement for an EFISHG measurement. The focused fundamental YAG laser beam ($1.06\mu\text{m}$) passes through a cell, shown in Figure 4.10b, which contains the solution. This consists of a stainless steel cylinder with two open slits into which are glued two, highly polished glass windows. In addition to allowing the input beam to pass through the solution, these sections define a wedge-shaped gap within the cylinder. The wedge angle is typically 0.3 degrees. The cell is translated in a horizontal direction normal to the laser beam such that the optical path length changes and several coherence lengths are encompassed within a

(a)



(b)

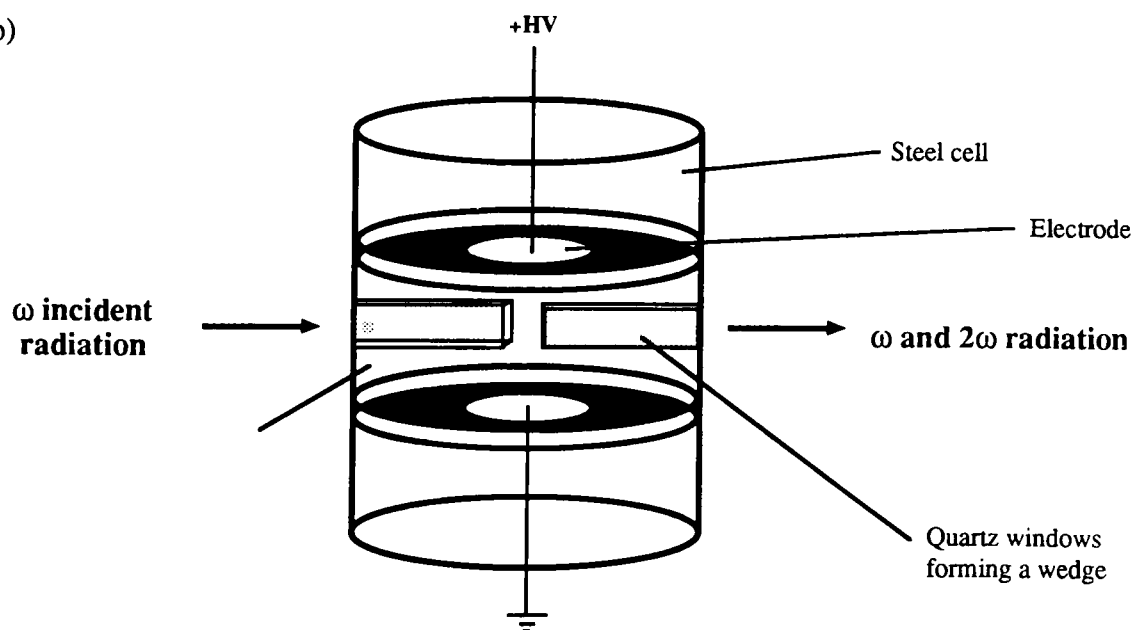


Figure 4.10 : (a) A schematic diagram of the experimental set-up for the measurement of non-linear optical molecular hyperpolarisabilities using the EFISHG technique and (b) a diagram of the cell which contains the solution under investigation.

single measurement. High voltage pulses of up to 10kV in amplitude are applied across the cell and, since the spacing between the top and bottom electrodes is known, the magnitude of the electric field is well defined. This field statistically aligns the solute molecules so that they can then interact with the optical field of the YAG laser beam to produce a frequency-doubled output. This signal is averaged and the amplitude of the second-harmonic output is recorded as a function of time.

The result is a set of fringes whose peak amplitude corresponds to a path length equal to an odd integer number of coherence lengths, and whose minima relate to an even number of coherence lengths. In order to estimate the magnitude of the non-linear response of the solute molecules, a recording of the fringes obtainable from a reference solvent must also be made. Acetone is normally chosen as many organic compounds are soluble in this solvent and its second-order non-linear properties have been thoroughly characterised. A direct comparison of the peak amplitude of the solution and acetone fringes enables the non-linearity of the solute to be assessed as indicated in Figure 4.11 . Normally, several different concentrations of solution are evaluated and an average value obtained. The expression for the third-order macroscopic susceptibility, $\Gamma_{nl}(x)$, contains the information needed to extract the second-order hyperpolarisability, β :

$$\Gamma_{nl}(x) = \frac{1}{l_c(x)} \left\{ 1.51 \left(\frac{I_{nl}(x) V_s}{I_s I_{nl}} \right) 10^{\left(\frac{D}{2}\right)} + 0.62 \right\} \quad (4.7)$$

where $I_{nl}(x)$ = the maximum amplitude of the solution fringes, I_s = the fringe amplitude of acetone, $V_{s,nl}$ = the electric field strength for the cell containing acetone and the solution respectively and D = the optical attenuation parameter. The coherence length $l_c(x)$ can be calculated from the interfringe spacing and the wedge angle which is itself measured using the acetone reference cell. That is:

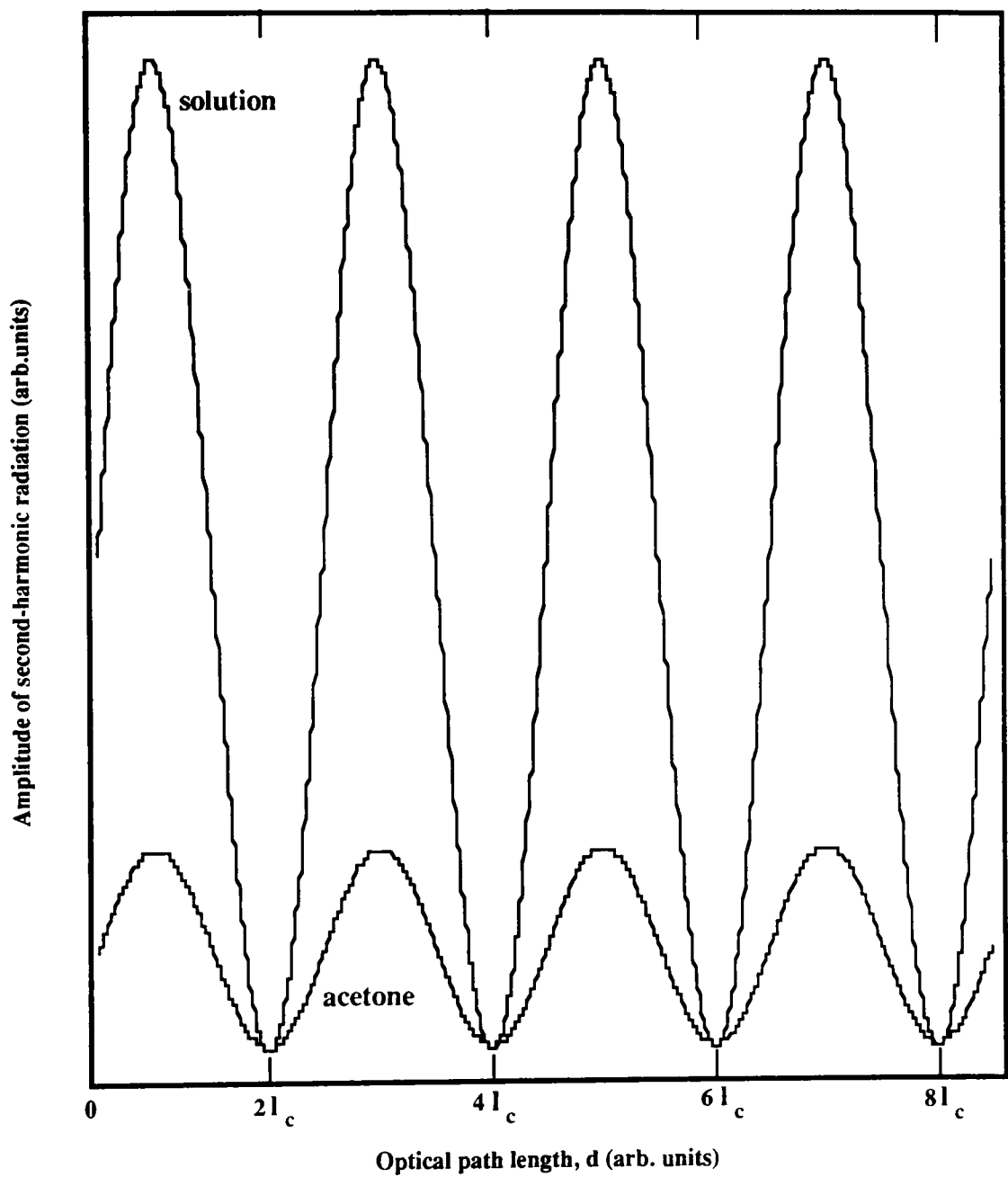


Figure 4.11 : The second-harmonic fringes produced as the optical path length is increased linearly for acetone and an acetone solution containing molecules possessing a significantly large second-order non-linear optical hyperpolarisability.

$$l_c(x) = \frac{1}{2} \delta \tan \phi \quad (4.8)$$

The coherence length of acetone is known to be 26.0 μm at a fundamental wavelength of 1.06 μm . Also:

$$\gamma_{nl} = \frac{M}{x\rho Nf} \{ \Gamma_{nl}(x) - \Gamma_s \} \quad (4.9)$$

where γ_{nl} = the third-order hyperpolarisability, ρ = the density of acetone which is 0.789 g ml^{-1} , N = Avogadro's number, f = the local field correction parameter and Γ_s = the third-order macroscopic susceptibility of acetone which is 8.2×10^{-14} esu. The units used in non-linear optics are discussed in Appendix B. It is most common to find the esu system in the literature and, for this reason, it is adopted here.

It can be seen that $\Gamma_{nl}(x)$ should be directly proportional to x , the mass concentration, where $x = m_{nl} / m_s$ in which $m_{s,nl}$ = mass of acetone and the solute per ml respectively. A plot of $\Gamma_{nl}(x)$ versus x should therefore yield a linear relationship. Finally:

$$\mu\beta = 5kT\gamma_{nl} \quad (4.10)$$

Therefore, a value of the product $\mu\beta$ can be found. Often, it is straightforward to estimate or measure the ground state dipole moment, μ , of a molecule which allows β to be derived. In this work, the EFISHG technique has been used to measure the products $\mu\beta$ of a range of cyano-terminated precursor compounds in order to investigate the relationship between the second-order optical properties and the detailed molecular structure of the compounds.

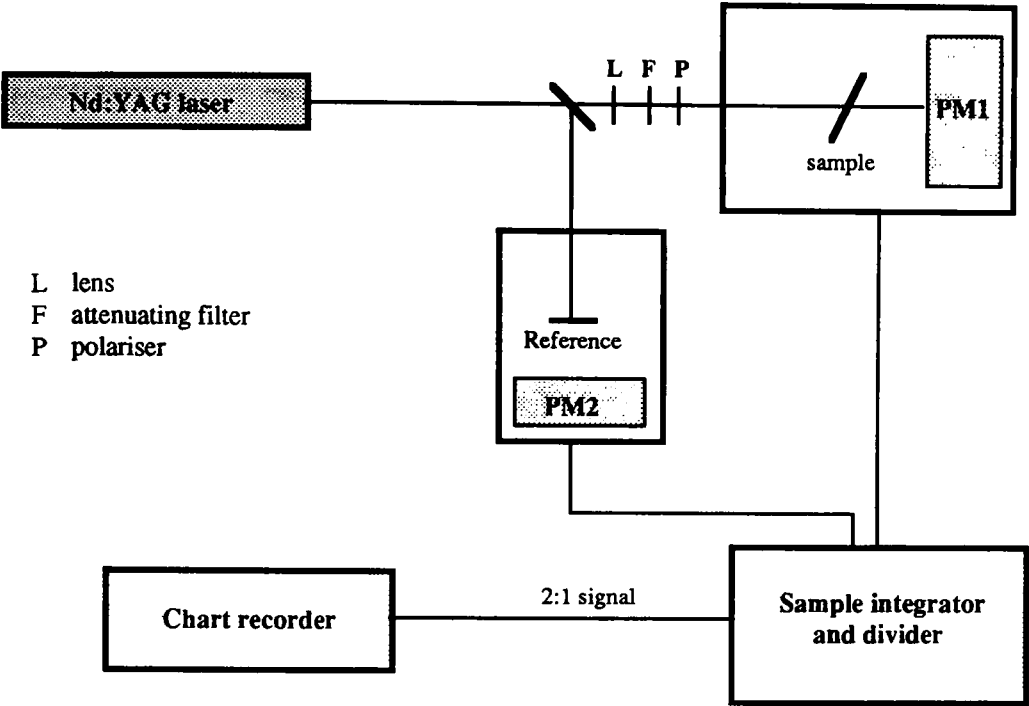
4.4.3 Second-harmonic generation (SHG) studies of monolayer and multilayer LB films.

The Langmuir-Blodgett technique is one of several methods used as a means of imposing a noncentrosymmetric crystal structure onto materials that often crystallise centrosymmetrically. In addition, the resulting high degree of alignment and packing density of the molecular dipoles within the monolayer or multilayer is unsurpassed by any other deposition or fabrication process. Second-order nonlinear optical characterisation of LB films [93,94] is usually achieved by measuring the second-harmonic signal emitted by the transferred LB film.

The signal intensity can be enhanced dramatically by the resonance effect, which has been discussed in Chapter 3, if either or both of the fundamental or second-harmonic wavelengths lie close to an absorption band within the material. Thus, many organic dyes have been studied whose absorption profiles easily encompass the second-harmonic wavelength so that the enhancement effect is large and extremely high values of hyperpolarisability are observed. Relatively thick films ($0.5 - 1.5\mu\text{m}$) are required, however, for integrated optics waveguiding applications. In the above case, the emitted second-harmonic signal is greatly attenuated by self-absorption. For this reason, many of the compounds studied in this research have been designed so that their absorption lies near to resonance but is reasonably small at the second-harmonic wavelength itself.

A schematic diagram of the apparatus used for the SHG experiments on LB films is shown in Figure 4.12a. The $1.064\mu\text{m}$ output from a $\text{Nd}^{3+}:\text{YAG}$ laser is used. Its polarisation direction can be changed using two quarter wave plates and the laser energy reaching the sample may be attenuated, if desired, with neutral density filters. The LB film

(a)



(b)

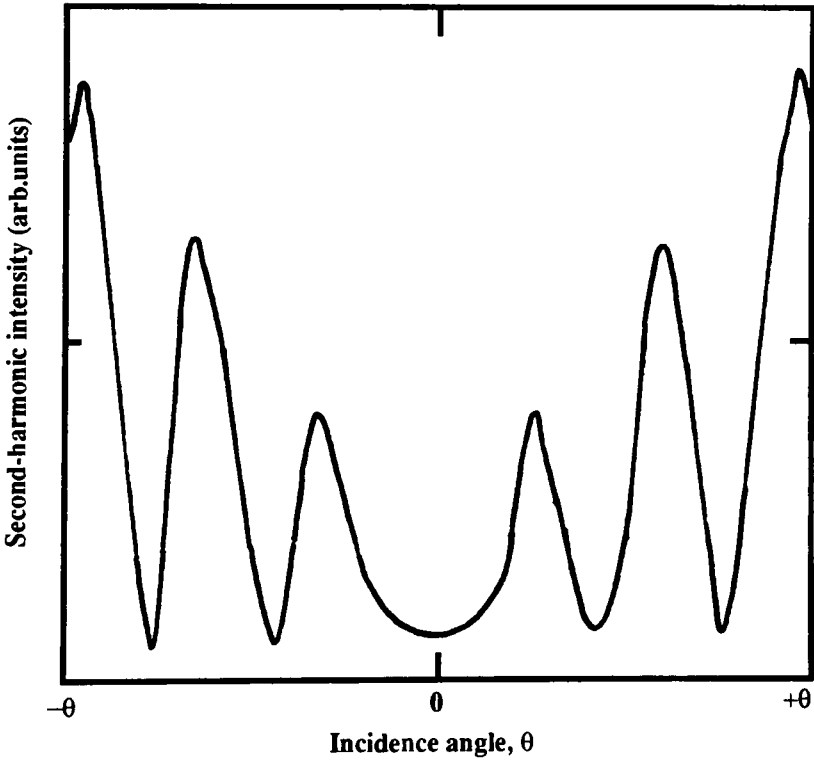


Figure 4.12 : (a) A schematic diagram of the apparatus used to measure the second harmonic conversion of LB films and (b) the fringe pattern obtained from layers coated onto both sides of a transparent glass plate.

sample is clamped securely onto a stepping motor - driven stage whose rotation axis is vertical and perpendicular to the incoming focused laser beam. The transmitted, unconverted beam is removed with suitable filtering. The second-harmonic signal is detected by a photomultiplier, averaged and recorded over an angle range of -50° to $+50^\circ$. The measurements are calibrated against the Maker fringes emitted from a 2mm thick quartz plate.

The input YAG beam is partially split such that a second "tributary" beam passed through a sample of the non-linear optical powder, N-4-nitro-phenyl-L-prolinol. Its frequency doubled radiation is detected by a second photomultiplier tube but sampled and averaged by the same lock-in amplifier as the 2ω signal exiting from the LB sample. In this way, it is possible to correct the data for laser fluctuations and therefore to improve the signal to noise ratio.

The emitted intensity from the LB film depends strongly upon the incidence angle of the incoming fundamental YAG beam. Indeed, a well-contrasted fringe pattern is produced, as shown in Figure 4.12b, which results from the interference between the harmonic beams produced by the front and back LB layers (in the case where both sides of the substrate are coated). The optical path length in the LB films is much smaller than the coherence length and therefore has no connection with Maker fringes. It originates from dispersion of the refractive index of the substrate, $n_s^{2\omega} - n_s^\omega$, which introduces a phase mismatch between second-harmonic waves generated at the front and back sides of the substrate. $n_s^\omega, n_s^{2\omega}$ are the fundamental and second-harmonic refractive indices of the glass substrate respectively. The dephasing factor varies with optical path length through the glass plate as it is rotated.

From the envelope function of the second-harmonic fringe pattern, the value of $\chi^{(2)}$ may be inferred. In practice, it is adjusted to give the best fit between the theoretical and

experimental envelope functions of the fringes. The second-harmonic intensity from the LB film can be written :

$$I_{LB}^{2\omega} = \frac{K_{LB} d}{\lambda^2} F(\chi^{(2)})^2 (E^\omega)^4 \cos \delta Q \quad (4.11)$$

where F includes factors related to the transmittance and reflectance of the various interfaces as a function of angles of incidence in the film and the substrate, and also on the several refractive indices. K_{LB} = a constant of the material and includes the absorption, E^ω = the electric field strength of the fundamental beam, and δQ is given by:

$$\delta Q = \frac{2\omega L}{c} (n_s^{2\omega} \cos \phi_s^{2\omega} - n_s^\omega \cos \phi_s^\omega) \quad (4.12)$$

$\chi^{(2)}$ values are determined by comparison of the amplitude of the interference fringes envelope with the signal from the quartz reference plate. This calibration eliminates the term $(E^\omega)^4$. The second-order molecular hyperpolarisability is deduced from the $\chi^{(2)}$ value on consideration of a molecular-oriented gas model in which:

$$\chi^{(2)} = N f^\omega f^{2\omega} \beta \quad (4.13)$$

$$\beta = \frac{\chi^{(2)} l}{f^\omega f^{2\omega} \sigma} \quad (4.14)$$

where $f^\omega, f^{2\omega}$ = Lorentz local field correction factors and $N = \sigma/l$ where σ = the surface density of molecules and l = thickness.

In this thesis, an attempt has been made to investigate the relationship between the second-order non-linearity and the electron donating and withdrawing substituents within the LB molecules in order to optimise their non-linear response.

4.4.4 Surface Plasmon Resonance.

Surface plasmon resonance (SPR) [95] is an extremely useful technique for the investigation of thin film overlayers on a highly reflecting metal film. Surface plasmon waves are collective oscillations of free charge at the boundary of a metal and a dielectric. The associated electric field is very large at the interface itself where propagation occurs and decays rapidly into the two adjacent media extending into the dielectric over a range of, typically, a few hundred nanometres. The behaviour of surface plasmons is, therefore, extremely sensitive to changes occurring at the interface. Thus, the technique is ideal for studying the properties of LB films owing to their thinness and homogeneity.

It is possible to deduce the refractive index and the thickness of such thin films using the experimental apparatus shown in Figure 4.13 a,b . The instrument is an Irlam Enterprise Surface Plasmon Resonance Reflectometer which is fully automated and controlled by an Archimedes 310 microcomputer. The system uses the Kretschmann configuration [96] for SPR excitation in which He-Ne laser light (633nm) is prism-coupled into a silver film. In practice, the silver film is evaporated onto a thoroughly cleaned Chance Propper microscope slide. The back of the slide is then brought into optical contact with the prism using index matching fluid (ethyl salicylate for BK7 prisms) so that the laser light observes no index change until coupling into the silver layer. The prism-sample arrangement is rotated so that the angle of incidence, θ , of the incoming He-Ne beam is varied. The detector also moves such that it always collects the reflected light from the sample stage. In several other SPR instruments, a simple θ – 2θ stage has been

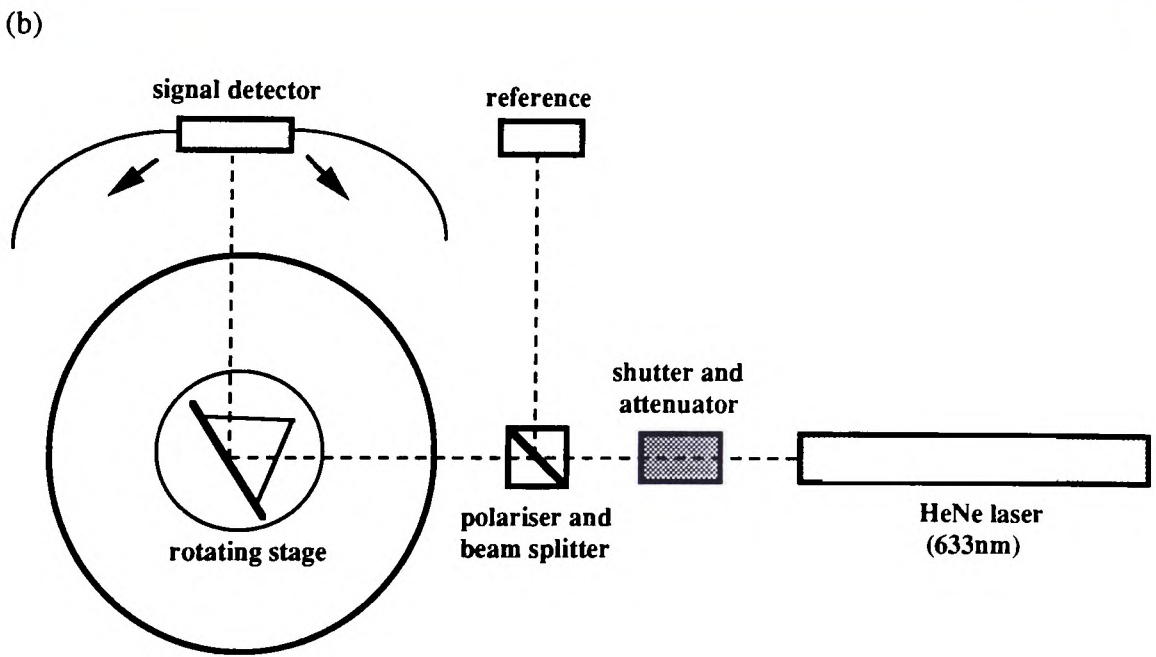


Figure 4.13 (a) A photograph of the surface plasmon resonance equipment used to measure the refractive index and thickness of thin LB films and (b) a schematic diagram showing its main components.

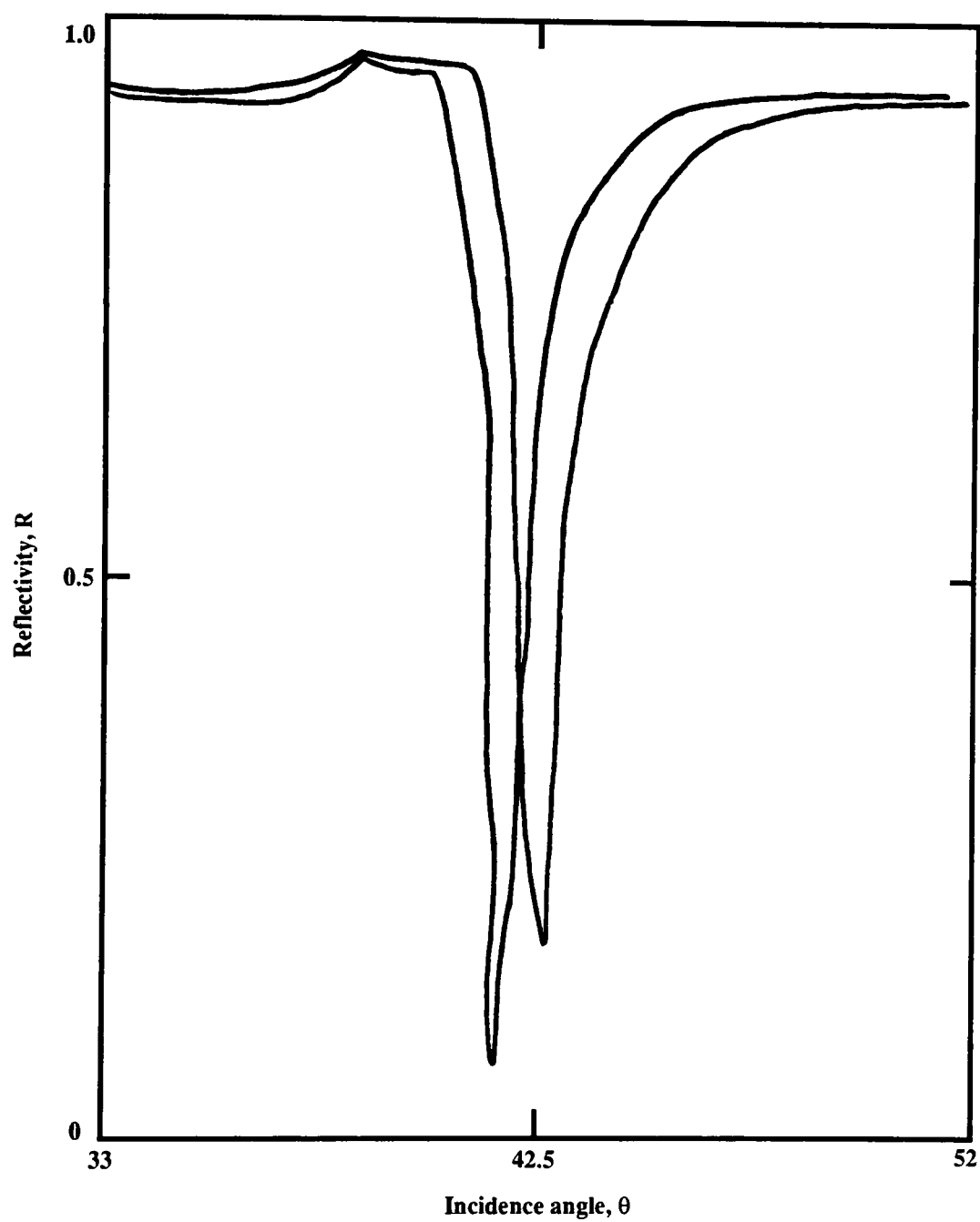


Figure 4.14 : Idealised surface plasmon resonance curves showing the shape of the resonance and the shift when a bare silver film is coated with a dielectric.

used to achieve this. However, in the system developed for the Oxford Laboratory, the prism-sample unit and the detector are independently driven in such a manner that a slight deviation from a θ – 2θ motion is implemented in order to account for beam walk-off. The reflectivity from the prism-sample arrangement is monitored as a function of angle. At a critical angle, the reflectivity falls dramatically as the photon energy excites the surface plasmon oscillations at the interface. The angular position and sharpness of the resonance is highly dependent upon the refractive index and the thickness of the dielectric. Figure 4.14 shows the reflectivity curve for a silver-air interface and the angular shift produced when a dielectric layer is deposited onto the silver.

In order to extract values of the absolute index of refraction and the film thickness of the LB film, it is necessary to fit the experimental data to computer generated theoretical reflectivity curves. This has been performed exhaustively at the Oxford Molecular Electronics Laboratory by Mr. S. Cooke [97] so that the instrument now yields useful and extremely accurate optical data. The instrument has been used in this work to perform preliminary studies on the organo-ruthenium complexes and, in particular, to examine the relationship between the refractive index and molecular structure.

4.5 Characterisation of thermal properties.

4.5.1 Pyroelectricity.

One of the main applications that has arisen from the study of the organo-ruthenium complexes, discussed in this research, is low-level thermal imaging. The range of uses of thermal cameras is vast and includes the defence weapons area, night and sea rescue, earthquake rescue and home security. A material whose molecules possess a net temperature-dependent dipole moment and can be arranged in a noncentrosymmetric

manner is pyroelectric. The theory has been discussed in Chapter 3 and only the experimental features will be described here.

The quasi-static measurement system is shown in Figure 4.15 . In order to detect a pyroelectric response, it is first necessary to heat the sample. The sample structure and electrode geometry is shown in Figure 4.15b . A Peltier heater is used which transfers heat energy between its upper and lower surfaces in response to the electrical current flowing through it. A Keithley 617 electrometer is used to monitor the short circuit current that flows when the temperature of the sample is altered and, therefore, when the normal component of the polarisation changes. The maximum amplitude of the current can be related to the pyroelectric coefficient by:

$$i_p = p A \frac{dT}{dt} \quad (4.15)$$

where i_p = the pyroelectric current, p = the pyroelectric coefficient, A = the electrode area and dT/dt = the rate of change of temperature. Therefore, only a rate of change of temperature produces a current in the device.

4.5.2 Thermal stability.

Some of the work in this thesis is concerned with improving the thermal stability of LB film molecules. The fatty acids and their derivatives are relatively unstable with melting points in the range 50 - 65 °C. For many applications, it is desirable to use materials with higher thermal stability.

The melting point of a given material is governed by the intermolecular interactions which bind the molecules in the crystal and determine their mutual orientation. For most

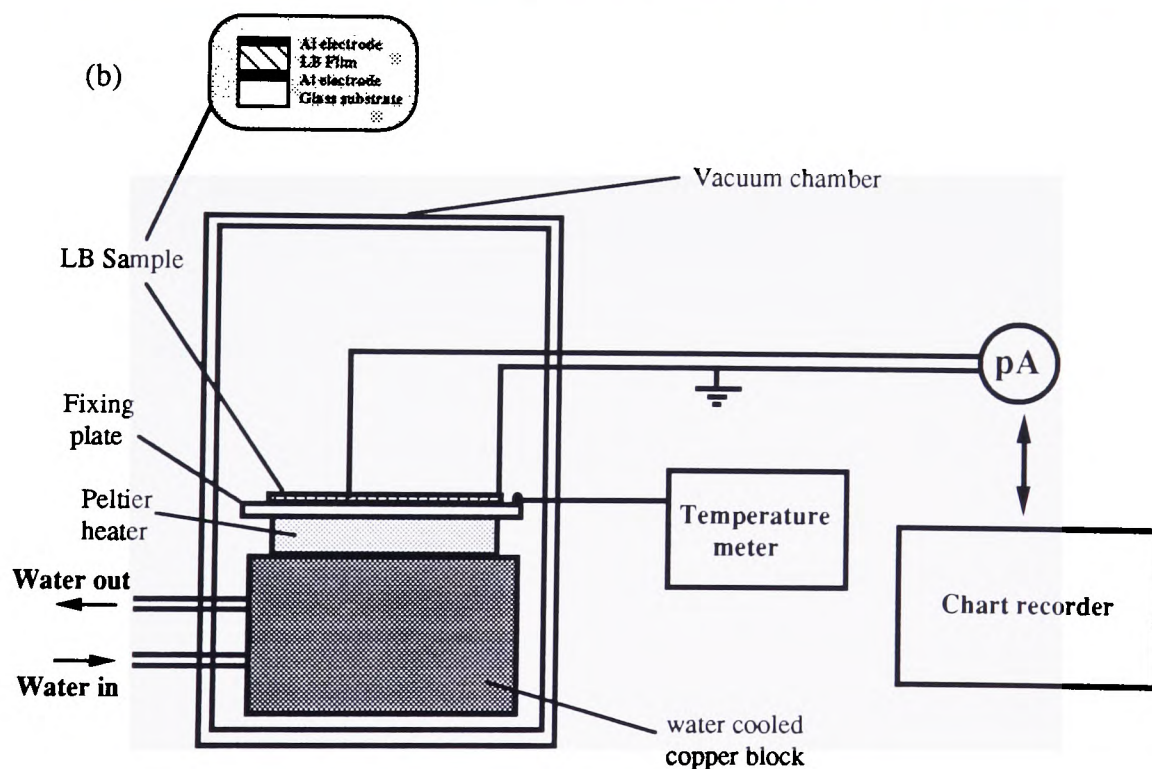
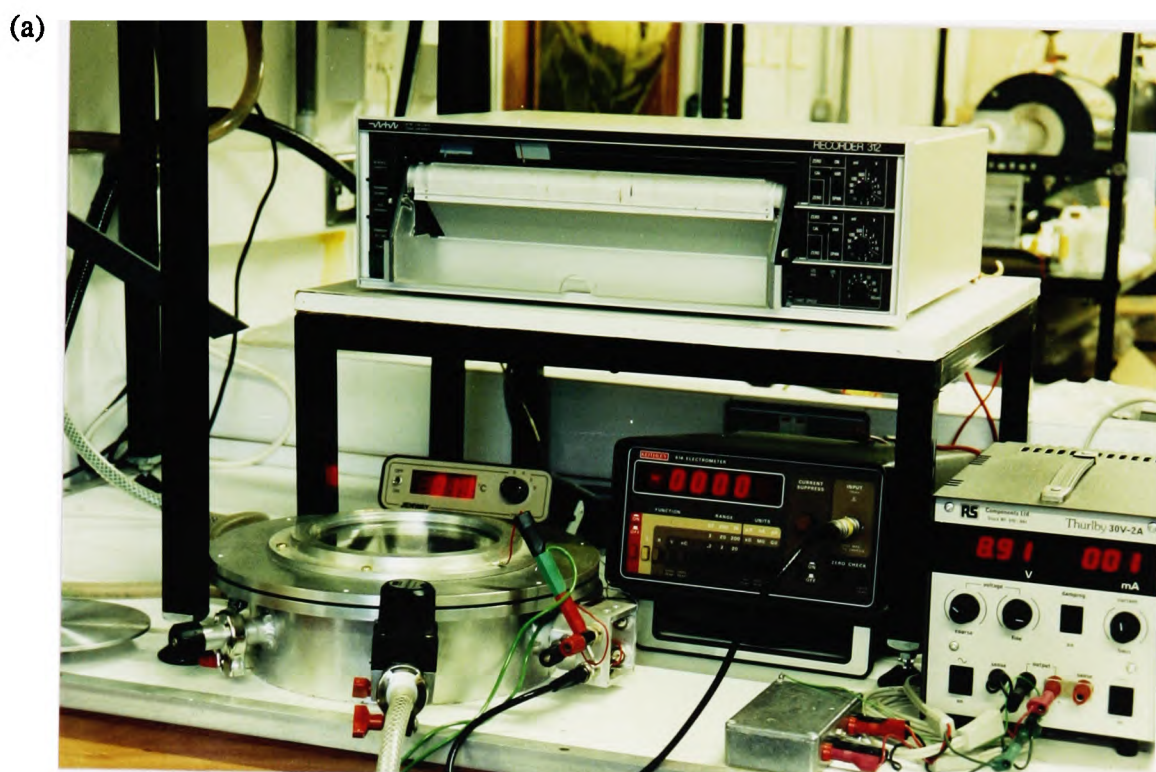


Figure 4.15 : (a) A photograph of the experimental apparatus used to measure the pyroelectric response of LB films and (b) a schematic diagram showing the principle of the measurement.

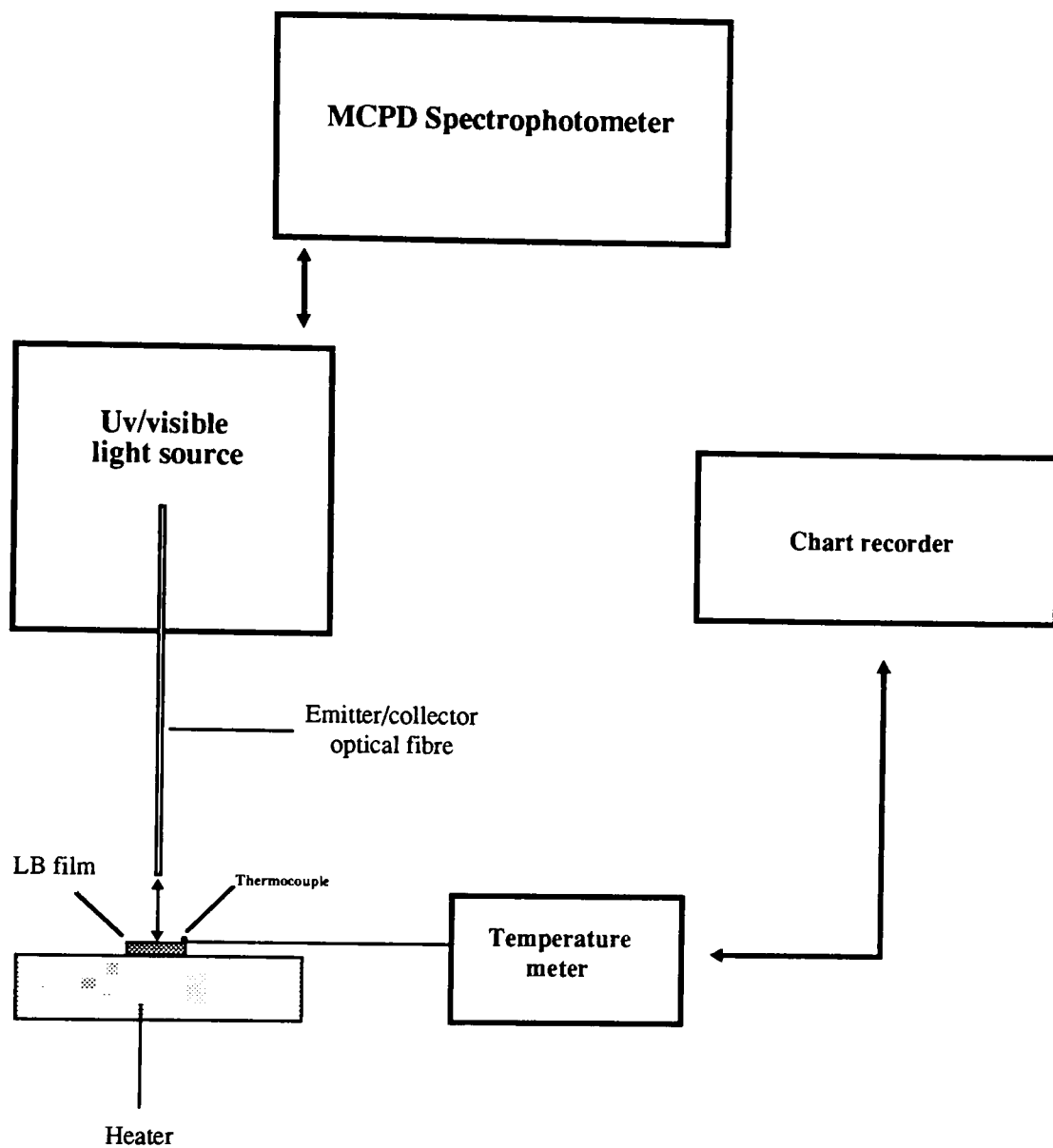


Figure 4.16 : The experimental arrangement for the testing of thermal stability in LB film samples using the MCPD spectrophotometer.

organics, the most important of these forces are van der Waals' and dipole-dipole interactions. In order to melt a solid, energy equivalent to the intermolecular binding energy associated with these forces must be supplied.

The bulk powder melting points can often yield useful information regarding the effect on thermal stability of both the molecular structure and the intermolecular packing forces which hold the molecules together in the crystal lattice. A Gallenkamp melting point apparatus has, therefore, been used to determine the thermal stability of the organo-ruthenium complexes and their precursors. The results of this study are discussed in Chapter 6.

The molecular architecture inside a bulk crystal is totally different to that within an LB film. It is, therefore, reasonable to expect to observe different thermal stability properties. In order to investigate this, an experimental system has been devised in which structural breakdown caused by heating the LB film can be observed. A schematic diagram of the apparatus is shown in Figure 4.16 .

The LB film must be deposited onto a highly reflecting surface such as aluminium, silver or silicon. The coated substrate is placed film upwards onto a Gallenkamp temperature controlled heater. The temperature is recorded as a function of time using a thermocouple as the film is slowly heated. The optical absorbance of the LB film is continuously monitored using the Otsuka Electronics MCPD-100 311C spectrophotometer discussed in Section 4.4.1 . In the geometry used, the emission fibre also collects the light reflected from the aluminium substrate having been partially absorbed by the LB film. The fibre is split such that the collected light is incident on the detector. Practically, the MCPD is programmed to record an absorption spectrum over the desired wavelength range, at a pre-determined interval (usually about 5s). Each spectrum is stored in the computer

memory. When the film undergoes a solid-liquid or solid-gas phase transition, the absorption spectrum changes drastically. This test has been used to study the factors that determine the thermal stability of the organo-ruthenium complexes in LB film form so that modifications to their molecular structure and deposition conditions can be made to further improve their stability characteristics.

4.6 Summary.

This chapter has included a description of the experimental techniques that have been used during the course of this work. The deposition of monolayer films can be assessed using a variety of techniques including quartz microgravimetric characterisation, uv-visible spectroscopy and electric-field induced second-harmonic generation for the non-linear optical properties. Several structural methods have also been mentioned with the intention of informing the reader of the available techniques for assessing LB films.

CHAPTER 5

Langmuir Film Properties of Novel Organo-Ruthenium Complexes.

5.1 Introduction.

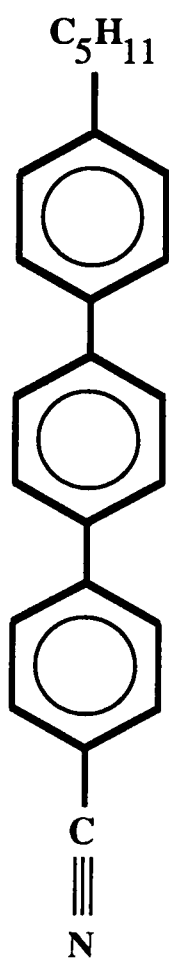
Many nitrile-terminated aromatic molecules possess the electron donor and acceptor groups and the electronic conjugation necessary to exhibit second-order non-linear optical and pyroelectric responses. Such compounds have been extensively studied because they often exhibit liquid crystalline phases [98]. In the case of 4-cyano-4'-n-pentyl-terphenyl, the nitrile group acts as an electron acceptor and the short pentyl chain behaves as an extremely weak electron donor. It is possible, however, to increase the strength of the donor by substitution with alkoxy or amine groups. These materials are therefore of great interest to the researcher wishing to examine the relationship between the second-order non-linear optical and pyroelectrical properties and their detailed molecular structure.

In order to systematically study the non-linear physics of such compounds, the type of the electronic conjugation and the strength of the donor and acceptor substituents should be varied. However, this approach is often complicated by the inability to produce the desired non-centrosymmetric structures of all the compounds under investigation. For example, few of the materials may crystallise acentrically and, therefore, an investigation into the generation of a second-harmonic optical wave from bulk single crystals yields

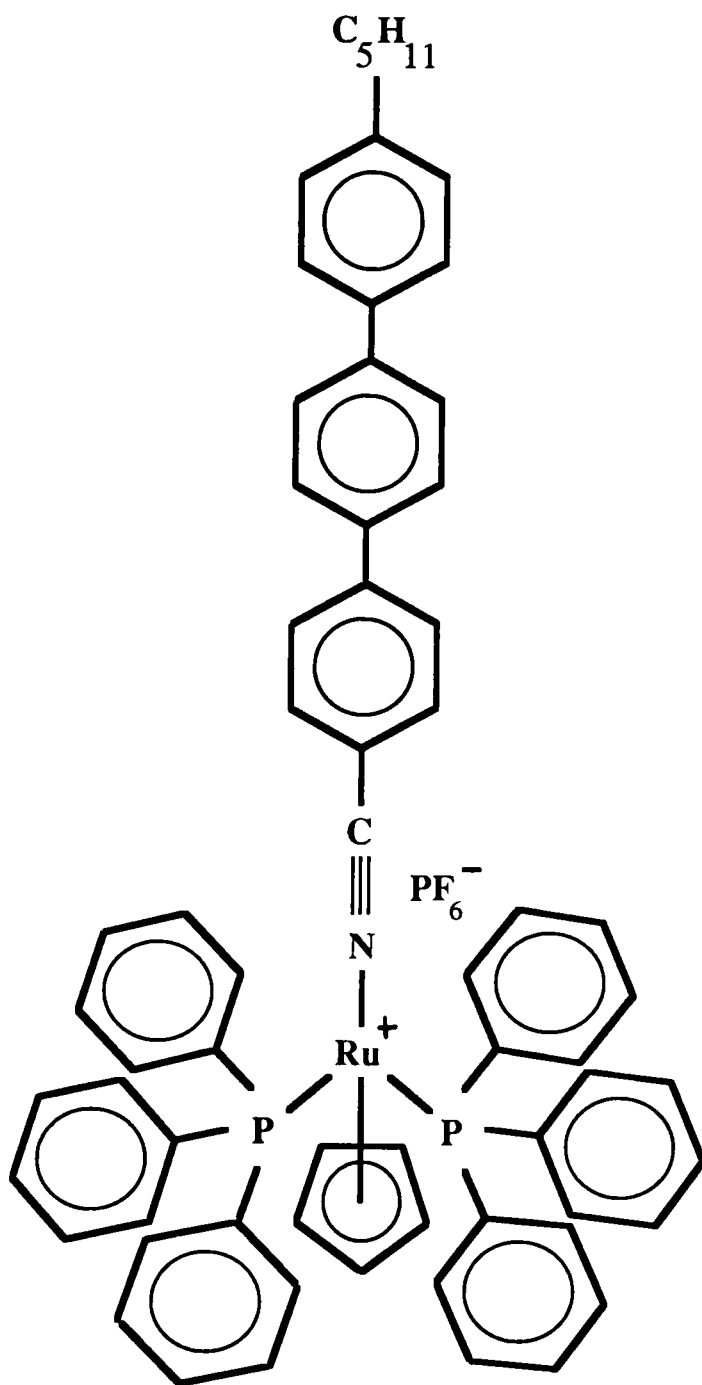
information only from those which adopt polar structures. EFISHG, which has been discussed extensively in chapter 4, partially circumvents this problem. However, only non-ionic compounds in solution are suitable. It is clear that a technique is required with which many materials within a particular group may be deposited in a reproducible manner such that the macroscopic symmetry conditions for second-order non-linear physical effects are satisfied.

The main purpose of the research discussed in this thesis is to systematically study a wide range of properties of a new class of intramolecular charge transfer compounds based upon the nitrile-terminated materials mentioned above. Although some of the nitrile compounds themselves (which will be referred to henceforth as 'precursor molecules') possess the necessary features for Langmuir film formation [99], transfer onto a solid substrate is extremely difficult and often impossible. However, in this work, it has been found that by complexing a ruthenium (cyclopentadienyl bis triphenylphosphine) hexafluorophosphate group to the nitrile group of the precursors, a novel class of organometallic complexes can be formed which universally form high quality Langmuir layers and can be deposited reproducibly using the LB process. As an example, the terphenyl compound shown in Figure 5.1a can be complexed to this ruthenium group to form the organo-ruthenium complex, N-ruthenium (cyclopentadienyl bis triphenylphosphine)-4-cyano-4'-n-pentyl-terphenyl hexafluorophosphate, shown in Figure 5.1b. This has enabled a systematic investigation of the Langmuir, LB and second-order non-linear properties of several intramolecular charge transfer compounds to be made.

In this particular chapter, the emphasis has been placed upon the preparation and characterisation of floating Langmuir films of the organo-ruthenium complexes. The predominant characteristics of the surface pressure - area isotherms and their dependence



(a)



(b)

Figure 5.1 : (a) A cyanoterphenyl compound and (b) the corresponding organo-ruthenium complex.

upon the subphase content and pH are discussed. A uv-visible spectrophotometer has been used to monitor the optical absorption properties as the spread monolayer is compressed. The areal stability at the air-water interface has been measured and accounted for by one or more possible contributing factors such as solubility in the subphase and monolayer collapse.

It is often necessary to spread a mixed solution containing two materials in order to improve the structural order within the Langmuir monolayer. Usually, one component of the mixture is a fatty acid compound which also improves the deposition efficiency. Such mixed layer studies will be discussed in section 5.5 followed by an account of novel two-component Langmuir monolayer studies in which certain organo-ruthenium complexes are mixed with their corresponding precursors [100]. Finally, it must be stressed that much preliminary work was required to discover the optimum ruthenium-based headgroup for the complexation onto the nitrile precursors. As the main body of research stemmed from this initial breakthrough, no detailed account is given of the experiments leading to this stage. Initially, a brief description of the chemical synthesis and the details of the nomenclature system used in the following sections will be given.

5.2 Synthesis of organo-ruthenium complexes.

The synthesis of the organo-ruthenium compounds described in this thesis involves three stages. The initial phase involves the synthesis of the precursor molecules themselves. This task is often complicated and may be approached using different synthetic routes for different compounds. As many precursors have been used here, the detailed procedures for each will not be given.

The second stage is concerned with the synthesis of ruthenium (η^5 -cyclopentadienyl)-(bis triphenylphosphine) chloride (**1**) which forms the organometallic reagent of the complexation reaction [101]. A filtered solution of hydrated ruthenium trichloride (0.52g) in dry ethanol (20ml) is added to a rapidly stirred solution of triphenylphosphine (2.1g) in refluxing ethanol (100ml). This is followed immediately by the addition of a solution of freshly distilled cyclopentadiene (1-2ml) in ethanol (20ml). The mixture is then refluxed for 45-60 minutes until the colour change from dark brown to orange is completed when it is cooled in a refrigerator for 12 hours. The orange crystalline product which separates is filtered, washed with cold ethanol (10ml) and dried to give pure ruthenium (η^5 -cyclopentadienyl)-(bis triphenylphosphine) chloride (1.25g, 86% yield, melting point 131-135°C).

Thirdly, the complexation reaction is initiated and occurs with high yield (>90%). The ruthenium (η^5 -cyclopentadienyl)-(bis triphenylphosphine) chloride is refluxed with the precursor compound with ammonium hexafluorophosphate in methanol, and, after chromatographic work-up, crystals of a novel stable salt are obtained. This reaction is represented in Figure 5.2 in which ϕ is a phenyl ring, R_{EC} is a conjugated electron system such as a phenyl ring, a *trans*-stilbene bridge or an azobenzene system and R_{ED} is an electron donating group such as $-OC_nH_{2n+1}$, NHC_nH_{2n+1} or $N(CH_3)C_nH_{2n+1}$. The complexation reaction occurs between the chloride (**1**) and an enormous range of nitrile precursors (**2**). It will be seen later that the ruthenium group effectively induces, in the precursor, the ability to form Langmuir films that are transferable onto a solid substrate. Indeed, the floating layer behaviour and the deposition properties are predominantly governed by the organo-metallic headgroup. Therefore, as large numbers of suitable precursor molecules can be synthesised, the complexation allows their physical properties, albeit somewhat modified by the ruthenium group itself, to be assessed in the same

material phase. Thus, problems that may arise with other techniques, such as the adoption of various crystal structures in single crystal growth, are avoided.

5.3 The nomenclature system.

The general formula for the class of organo-ruthenium compounds investigated is shown in Figure 5.2 (**3**). The naming policy is best described by listing the features. The sole ambiguity with the following system arises as the position of a substituent on a phenyl ring is not represented. However, without exception, all substituted groups occur in the *para* position for every precursor and corresponding ruthenium complex. The approach is not designed for broader use outside this field.

- (i) The ruthenium headgroup and the adjoining nitrile group occur in all the organo-ruthenium complexes studied. It is therefore sensible to represent these two groups simply by 'Ru'.
- (ii) The various conjugated electron systems all contain at least one phenyl ring which is written as ' ϕ '.
- (iii) Compounds containing two or more adjacent, directly bonded phenyl rings can be shown as ' ϕ_2 ' or ' ϕ_3 ' etc.
- (iv) Where there exists a bridging group between two phenyl rings, such as in the *trans* - stilbene and azobenzene molecules, this may be represented by ' $-C_2''-$ ' and ' $-N_2'''-$ ' respectively, where the subscript refers to the number of carbons or nitrogens in the bridge and the superscript corresponds to the covalent bond between each carbon or each nitrogen; that is, a '' means a double bond and a ''' means a triple bond.

- (v) The donor group is simply expressed as ' $-\text{OC}_n$ ' for an alkoxy group consisting of a carbon chain $\text{C}_n\text{H}_{2n+1}$, or ' $-\text{NMe}_2$ ' for a dimethylamine group.
- (vi) If the floating or deposited film is a mixed, two-component monolayer, then both components must be represented. This done easily by writing ' A^x / B^y ' where A and B are the individual component materials and x and y are the composition ratios. For example $\text{Ru}-\phi-\text{C}_2''-\phi-\text{OC}_{13}^{50} / \text{Behenic}^{50}$ represents a mixed 1:1 system containing $\text{Ru}-\phi-\text{C}_2''-\phi-\text{OC}_{13}$ and behenic acid.
- (vii) When the precursors are referred to, the nitrile group is included. For instance, 4-cyano-4''n-pentyl-p-terphenyl can be shortened to $\text{NC}-\phi_3-\text{C}_5$.

Table 5.1 shows the molecular structure and the abbreviated names of all the organo-ruthenium complexes using the nomenclature explained above.

5.4 Preparation of Langmuir films of organo-ruthenium complexes.

This section details the procedures involved in the preparation of high quality organo-ruthenium monomolecular Langmuir layers on a pure water (Milli-Q) subphase using a single layer Langmuir trough.

5.4.1 Solvent solubility and solution characterisation.

In order to produce a floating film, it is necessary to use a spreading solution and it is therefore instructive to characterise the salient features of the solute in this form. The molecules of the organo-metallic complex must be dispersed uniformly across the entire

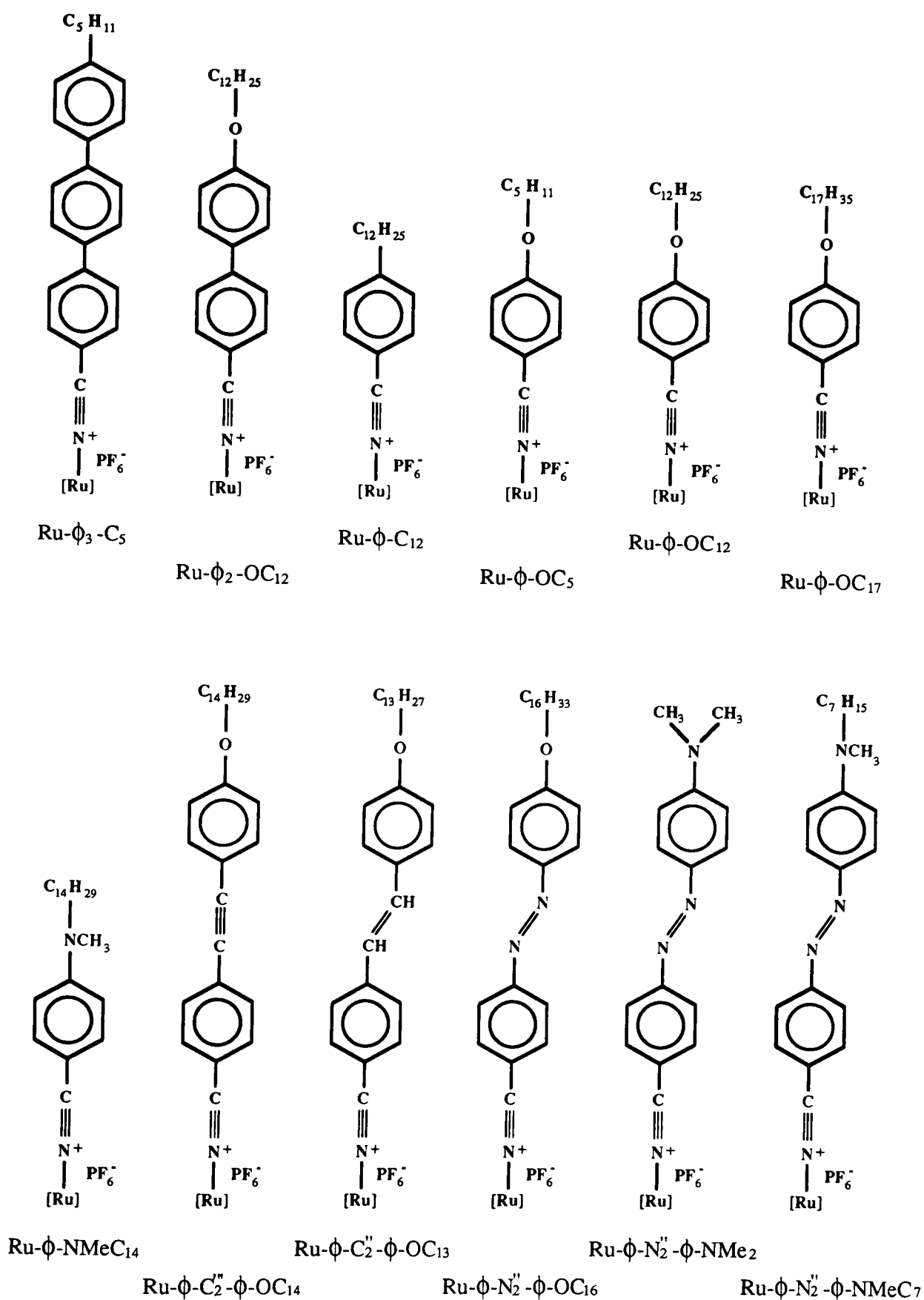


Figure 5.3 : The organo-ruthenium complexes studied in this research.

available water surface. To achieve this, a suitable spreading solvent is required. It is also an advantage if the spreading solvent actually dissolves the solute molecules so that a second solvent is not needed for this purpose. Chloroform has been used extensively for the compounds discussed in this thesis as they are readily soluble and the solvent spreads spontaneously on contact with water thus distributing the solute evenly over the surface. In addition, its moderate evaporation rate allows complete spreading to occur before it evaporates entirely, although it does not remain locked into the monolayer like other solvents such as 1,3-dimethylbenzene (xylene) or 1,3,5-trimethylbenzene (mesitylene) which are extremely involatile. Finally, chloroform is immiscible with water thus ensuring that no solute molecules are drawn into the bulk subphase unlike acetone which shows this tendency. In section 5.4.4, it will be seen that the concentration of the spreading solution can have a dramatic effect upon the Langmuir and LB film properties. Typically, however, a concentration of 0.1 - 0.2 mgml⁻¹ (10⁻⁴M) is used.

It is important to characterise the optical absorption properties of the solution for four main reasons which are outlined below:

(a) It is essential that the solute molecules are chemically stable in the chosen solvent(s) for as long a period of time as possible in order that the spread monolayer properties correspond to the original compound dissolved and not to an oxidised or reduced species. If this is not the case a freshly prepared solution must be made before each set of experiments. This is wasteful of material although often necessary. Another approach is to use a concentrated solution containing a solvent which does not affect the solute at all from which dilute spreading solutions can be routinely prepared using the chosen distribution solvent which makes up a large proportion of the total solvent content. In order to prevent photochemical influences, all solutions were protected from the light by wrapping the flasks in aluminium foil.

(b) Certain materials form molecular aggregates in solutions of high concentration [102] which may often exhibit very different physical and chemical properties from the monomer in dilute conditions. Because the LB deposition technique imposes a high packing density of molecules (equivalent to concentration) in both the floating and transferred films, it is important to establish the existence or otherwise of dimeric or trimeric species. Examination of solutions of the material under investigation of increasing concentration often gives an insight into such aggregation effects. In Chapter 4, the presence of dimers of a metal-substituted phthalocyanine molecule was described with reference to Figure 4.7. All of the organo-ruthenium complexes, however, were found not to exhibit these effects as exemplified by complex Ru- ϕ -N₂^{''}- ϕ -NMe₂ in Figure 5.4 .

(c) Uv-visible spectroscopy may be used to measure the exact concentration of a spreading solution. When the small amount of product is weighed with a standard laboratory balance (Ohaus Model 160), the accuracy of the reading is approximately ± 0.1 mg. However, if great care is initially taken to prepare a solution of exact known concentration, then a Beer-Lambert investigation yields an accurate molar extinction coefficient (molar absorptivity). Future solutions may be assessed spectrally and the concentration inferred from the original Beer-Lambert plot. Such an approach also circumvents problems that may occur due to dissolution of the solute.

(d) Finally and most importantly, for many applications, it is vital to know the shape of the absorption band and the wavelength at which maximum absorption occurs (λ_{max}). For example, in the field of second-order non-linear optics, the efficiency of conversion from a fundamental laser frequency to a doubled frequency output is critically dependent on the position of λ_{max} because of the resonance enhancement of the second-order non-linear optical hyperpolarisability, β_{CT} [103]. The relationship between the uv-visible absorption properties and the intricate molecular structure can offer an exciting means of assessing the

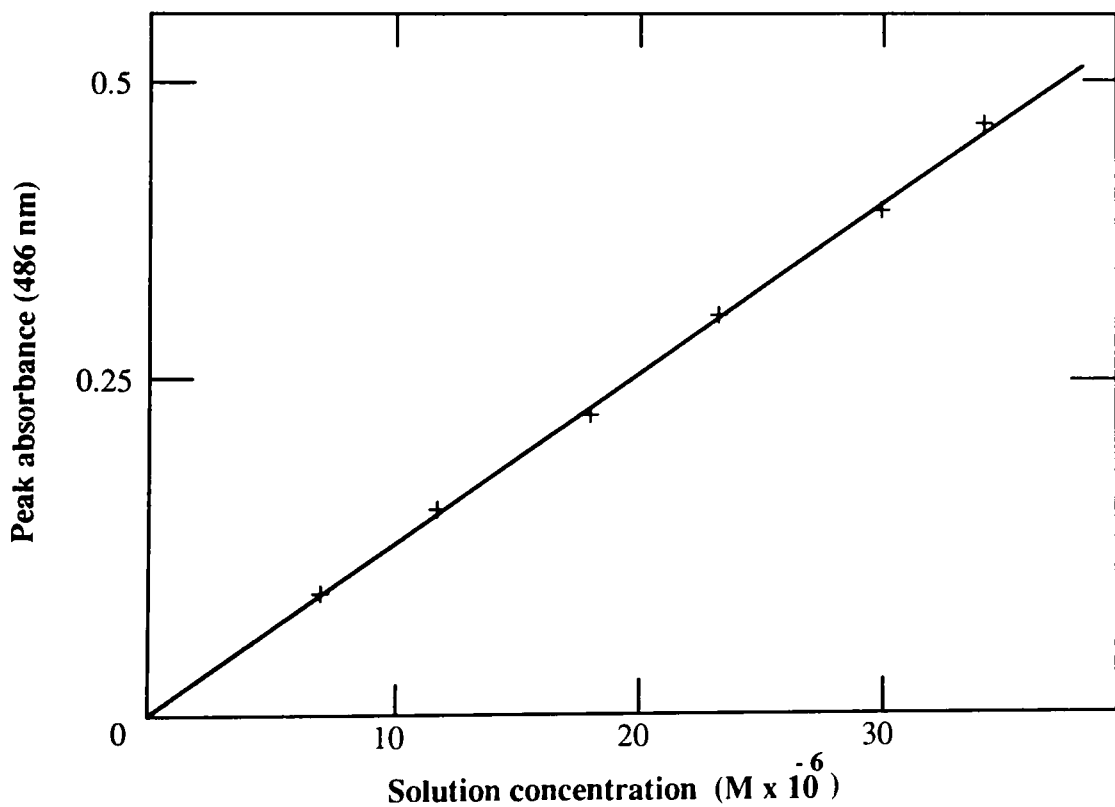
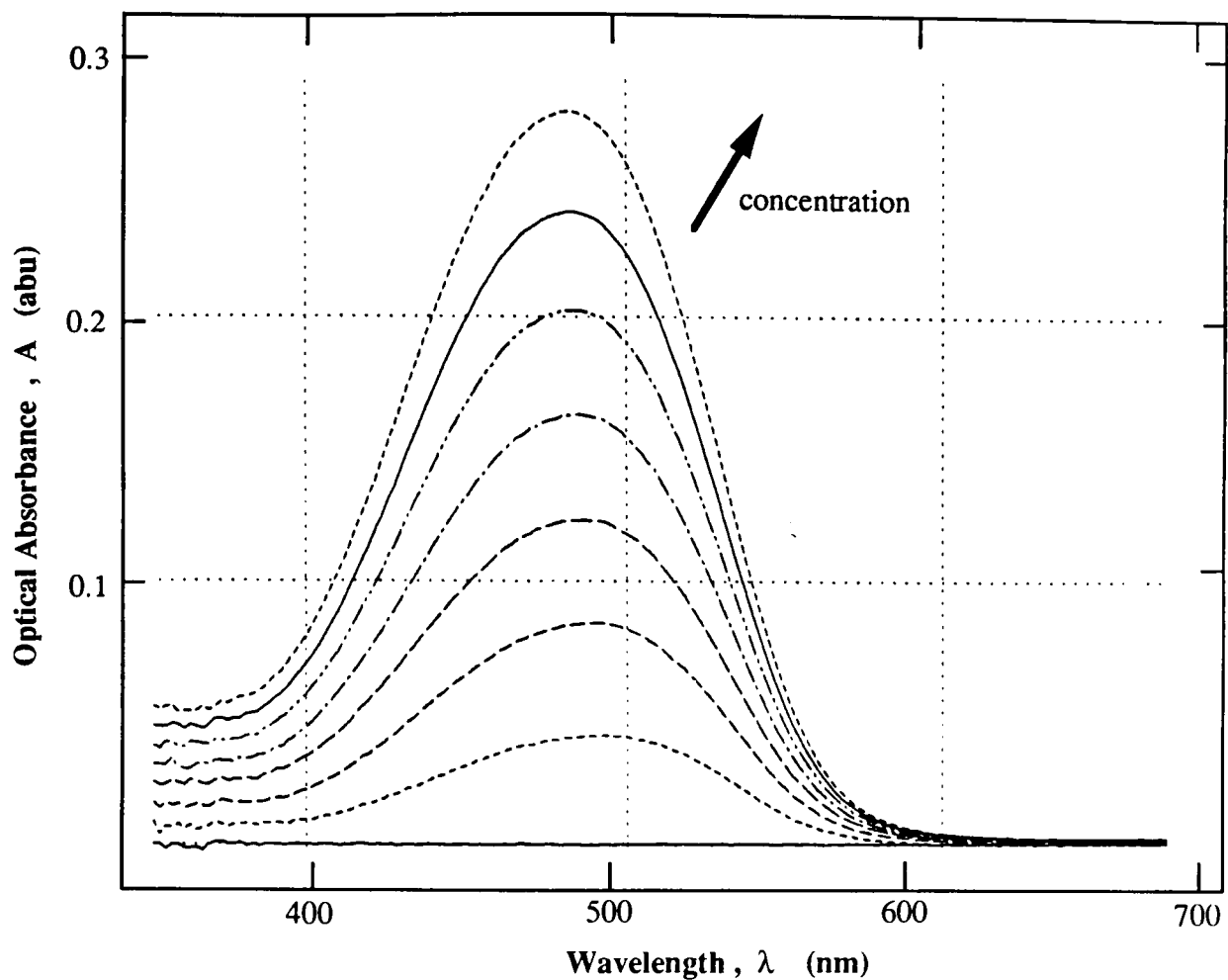


Figure 5.4 : Verification of the Beer-Lambert law for a solution of Ru-φ-N₂²⁺-φ-NMe in chloroform: (a) electronic absorption spectra versus wavelength for various concentrations and (b) the peak absorbance versus concentration plot.

potential use of a compound for non-linear optics applications. In addition, it is also often instructive to compare the absorption spectra of solutions with those of the floating Langmuir and deposited LB layers. The resulting shifts in the position of $\lambda_{\max}$ yield useful information concerning the alignment of dipolar molecules. Such data will be presented later in this chapter.

Table 5.1 gives the position of $\lambda_{\max}$ and the molar extinction coefficient $\epsilon_{\max}$ for all of the ruthenium complexes studied to date and for some of the precursors. Each figure presented has been obtained from a Beer-Lambert plot which displayed an accurately linear relationship in all cases. These results will be discussed with relevance to EFISHG behaviour of the precursors in Chapter 7 although the main features of the solution spectra will be outlined below in order to give a flavour of the spectroscopic properties of the class of materials studied.

The position of the $\lambda_{\max}$ wavelength, as the strength of the donor and acceptor groups increases, progressively shifts toward the red end of the spectrum. It can be seen, for instance, that the strong dimethylamine group induces an enormous 104nm shift relative to the weaker hydroxyl group for the ruthenium-complexed azobenzene molecules, Ru- ϕ -N₂"- ϕ -NMe₂ and Ru- ϕ -N₂"- ϕ -OH. Indeed, a series of donor groups of increasing strength may be extracted from this data for several types of conjugated electron systems. The complexes possessing a single phenyl ring for the conjugation show a progressive bathochromic shift for the series Ru- ϕ -C₁₂ < Ru- ϕ -OC₁₂ < Ru- ϕ -NH₂ < Ru- ϕ -NMeC₁₇ which is consistent with the donor strength increasing in the order -C₁₂ < -OC₁₂ < -NH₂ < NMeC₁₇. It is interesting to note that no change in $\lambda_{\max}$ is observed when the length of the carbon chain is increased on the alkoxy compounds Ru- ϕ -OC_n although a fairly large shift (28nm) occurs for the long chain substitution of the amide group of Ru- ϕ -NMeC₁₇. Clearly, the wavelength changes are not additive; a doubling of

Table 5.1 : Uv-visible spectroscopic data for organo-ruthenium complexes and their precursors.

Precursor	λ_{max} solution nm	ϵ_{max} solution $\times 10^3$ $\text{mol}^{-1} \text{l cm}^{-1}$	Ruthenium Complex	λ_{max} solution nm	ϵ_{max} solution $\times 10^3$ $\text{mol}^{-1} \text{l cm}^{-1}$
$\text{NC}-\phi_3-\text{C}_5$	303	39.0	$\text{Ru}-\phi_3-\text{C}_5$	307	61.7
$\text{NC}-\phi_2-\text{OC}_{12}$	295	28.8	$\text{Ru}-\phi_2-\text{OC}_{12}$	332	29.0
$\text{NC}-\phi-\text{C}_{12}$	232 *	-	$\text{Ru}-\text{NC}-\phi-\text{C}_{12}$	314	-
$\text{NC}-\phi-\text{OC}_3$	247 *	-	$\text{Ru}-\phi-\text{OC}_3$	300	17.9
$\text{NC}-\phi-\text{OC}_5$	-	-	$\text{Ru}-\phi-\text{OC}_5$	300	17.1
$\text{NC}-\phi-\text{OC}_{12}$	-	-	$\text{Ru}-\phi-\text{OC}_{12}$	300	17.0
$\text{NC}-\phi-\text{OC}_{17}$	-	-	$\text{Ru}-\phi-\text{OC}_{17}$	300	18.1
$\text{NC}-\phi-\text{NH}_2$	269 *	-	$\text{Ru}-\phi-\text{NH}_2$	309	24.1
$\text{NC}-\phi-\text{NMeC}_{14}$	300	18.6	$\text{Ru}-\phi-\text{NMeC}_{17}$	337	-
$\text{NC}-\phi-\text{C}_2'''-\phi-\text{OC}_{14}$	321	22.1	$\text{Ru}-\phi-\text{C}_2'''-\phi-\text{OC}_{14}$	355	30.2
$\text{NC}-\phi-\text{C}_2''-\phi-\text{OC}_{13}$	344	29.5	$\text{Ru}-\phi-\text{C}_2''-\phi-\text{OC}_{13}$	368	31.4
$\text{NC}-\phi-\text{N}_2''-\phi-\text{OH}$	367	22.1	$\text{Ru}-\phi-\text{N}_2''-\phi-\text{OH}$	382	23.2
$\text{NC}-\phi-\text{N}_2''-\phi-\text{OC}_{16}$	-	-	$\text{Ru}-\phi-\text{N}_2''-\phi-\text{OC}_{16}$	383	17.2
$\text{NC}-\phi-\text{N}_2''-\phi-\text{NMe}_2$	451	17.7	$\text{Ru}-\phi-\text{N}_2''-\phi-\text{NMe}_2$	486	35.7
$\text{NC}-\phi-\text{N}_2''-\phi-\text{NMeC}_7$	462	24.7	$\text{Ru}-\phi-\text{N}_2''-\phi-\text{NMeC}_{17}$	498	41.8

* From A. Dulcic, C. Sauteret J. Chem. Phys. 69 (8), 15 Oct. 1978.

the donor strength will not necessarily produce a two-fold increase in the wavelength shift. Indeed, the greatest shift would be expected if the donor *and* the acceptor are both strongly active as the perturbation to the molecular energy levels depends not only on the distortion of the conjugated electron density caused by each substituent individually, but also that which arises owing to the charge transfer interaction [104] of the substituents.

Another important conclusion that may be drawn from the data in Table 5.1 is the effect on the spectra of the various types of conjugation. The majority of the compounds are alkoxy substituted. They can therefore be used to examine the resultant energy level perturbations brought about by changing the conjugation *alone* whilst maintaining fixed donor (alkoxy) and acceptor (ruthenium-nitrile) groups. Also, it has been pointed out that the variation in the length of the carbon chain has little or no effect upon the λ_{max} value in solution for this sub-class of complexes. Therefore, the variation in chain length can be neglected in terms of spectroscopic properties in this case. It can be seen that the red-shift increases in the series Ru- ϕ -OC₁₂ (300nm) < Ru- ϕ_2 -OC₁₂ (332nm) < Ru- ϕ -C₂'''- ϕ -OC₁₄ (355nm) < Ru- ϕ -C₂''- ϕ -OC₁₃ (368nm) < Ru- ϕ -N₂''- ϕ -OC₁₆ (383nm). Therefore, the order in which electron density is made available for substituent distortion by the various conjugation systems is - ϕ - < - ϕ_2 - < - ϕ -C₂'''- ϕ - < - ϕ -C₂''- ϕ - < - ϕ -N₂''- ϕ - . This data is shown diagrammatically in Figure 5.5 .

The complex showing the highest absorption wavelength is Ru- ϕ -N₂''- ϕ -NMeC₁₇. This is a direct consequence of the mutual presence of the strong donor and acceptor substituents and the azobenzene conjugation.

The addition of the ruthenium (η^5 -cyclopentadienyl)-(bis triphenylphosphine) group itself induces a shift typically of the order of 30nm relative to the corresponding precursor molecule. This effect is shown by virtually all the complexes in Table 5.2 and suggests a

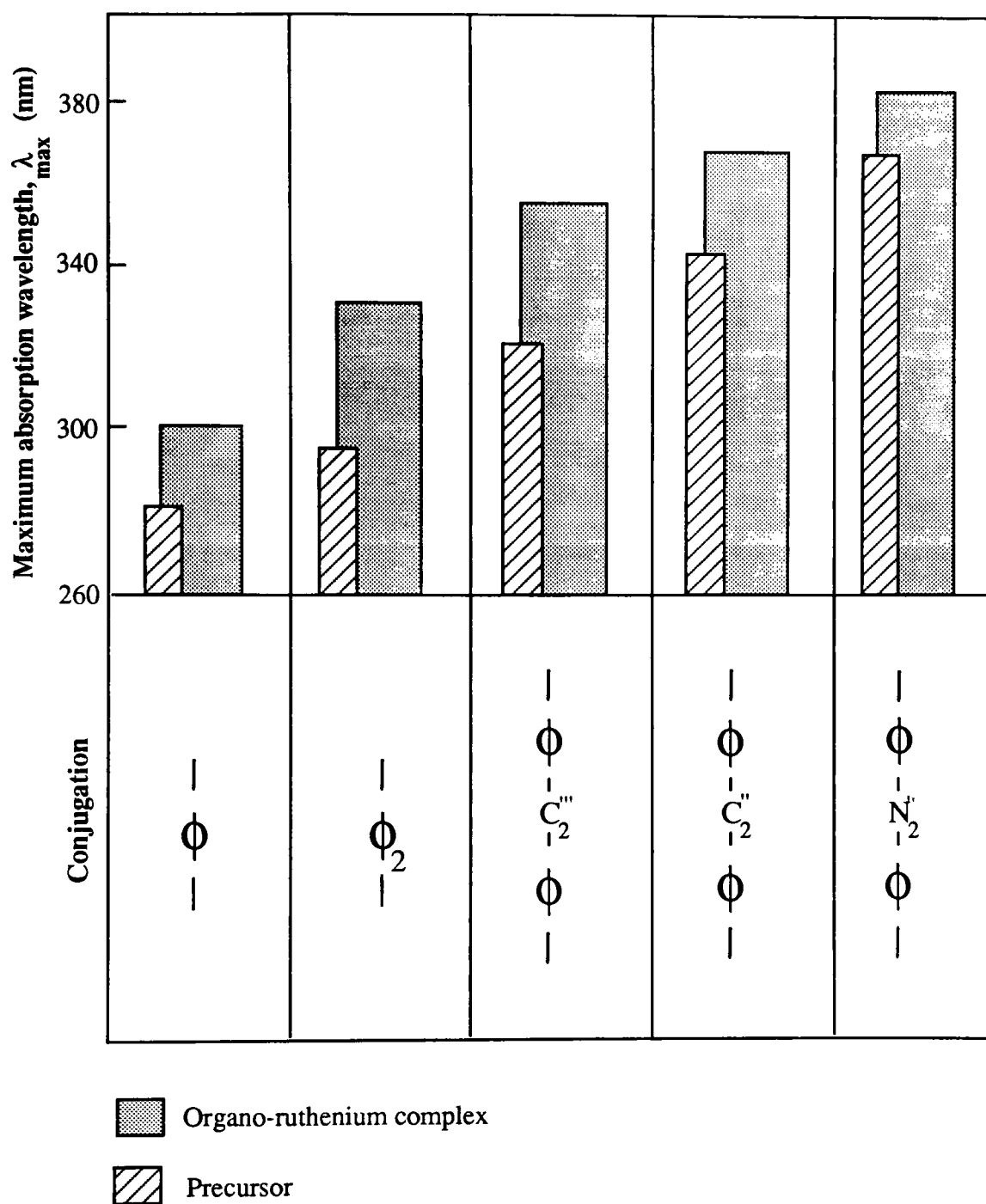


Figure 5.5 : The effect of the electronic conjugation on the uv-visible absorption of complexes of the general formula $\text{Ru} \text{---} \text{R}_{\text{EC}} \text{---} \text{OC}_n$ and their precursors.

significant enhancement of the acceptor strength of the ruthenium-nitrile grouping relative to the simple nitrile acceptor of the precursors. Indeed, reference to the literature [105] allows the novel ruthenium acceptor (Ru) to be listed in a series of increasing electron withdrawal such that $-\text{CN} < -\text{CHO} < -\text{COCH}_3 < -\text{Ru} < -\text{NO}_2$.

The variation of the molar extinction coefficient for the organo-ruthenium complexes and precursors is also interesting. Very approximately, the absorptivity can be seen to increase as the number of phenyl rings in the conjugated electron system increases. Thus, for ruthenium-substituted single phenyl ring compounds with alkoxy donors ϵ_{max} is about $17 \times 10^3 \text{ mol}^{-1} \text{ l cm}^{-1}$ and for $\text{Ru}-\phi-\text{C}_2'''-\phi-\text{OC}_{14}$ and $\text{Ru}-\phi-\text{C}_2''-\phi-\text{OC}_{13}$ the coefficients are approximately doubled. In addition, they tend to be larger for the ruthenium complexes relative to the precursors.

This section has stressed the importance of the characterisation of the materials of interest in solution form in order to investigate the solubility in various solvents, the uv-visible spectroscopic properties and the spreading behaviour over a water surface.

5.4.2 Preparation and compression of organo-ruthenium monolayers.

The floating Langmuir films of the novel complexes are prepared by carefully applying a small quantity of dilute solution dropwise onto the surface of a cleaned, highly pure water surface. A Hamilton microsyringe, whose total volume is typically 500 μl , is used, each drop containing approximately 4 μl of spreading solution. A few seconds is allowed to elapse between drops to achieve complete distribution of the solute and likewise each application occurs in a different position on the surface. Finally, a few minutes lapse to enable total evaporation of the spreading solvent (chloroform).

The organo-ruthenium layer is now in a state in which there is little or no order awaiting manipulation. The barriers of the single layer Langmuir trough are brought together such that the rate of area decrease is approximately $3.0 \text{ cm}^2 \text{ s}^{-1}$. The surface pressure within the layer is monitored using a Wilhelmy plate arrangement and is plotted as a function of the total area occupied by the film using an x-y chart recorder. The detailed structure of the surface pressure - area isotherms of the ruthenium Langmuir films show several distinctive features and subtle differences occur for each complex. Figure 5.6 attempts to show the most striking characteristics.

The precursor $\text{NC-}\phi_3\text{-C}_5$ is readily available from several chemical manufacturers, and for this reason, the first organo-ruthenium complex synthesised was $\text{Ru-}\phi_3\text{-C}_5$. Its isotherm is shown in Figure 5.6a. Initially, as the area available to the floating layer is reduced, the molecules are well separated and no significant intermolecular interactions occur thus causing no change in surface pressure. This state of the layer can be compared to a gas phase in which intermolecular forces are extremely weak. However, as the film is compressed further, the average distance between adjacent molecules decreases and van der Waals' and dipole-dipole interactions begin to play a significant role in determining the structure and order within the film. Such interactions induce a change in surface pressure of the film which can be seen to initially rise very gradually. The intermolecular forces are now dominant but are nevertheless changing as the layer is still compressible. Further reduction in the area produces an increasingly dramatic increase in surface pressure which rises steeply from around 5 mNm^{-1} and above. In this region, the molecules are tightly packed and the film is only slightly compressible. In this phase it behaves as a two-dimensional floating solid layer.

The point at which the steep incline of surface pressure begins to fall off signifies the onset of some change in the structure of the Langmuir film. This could either be a

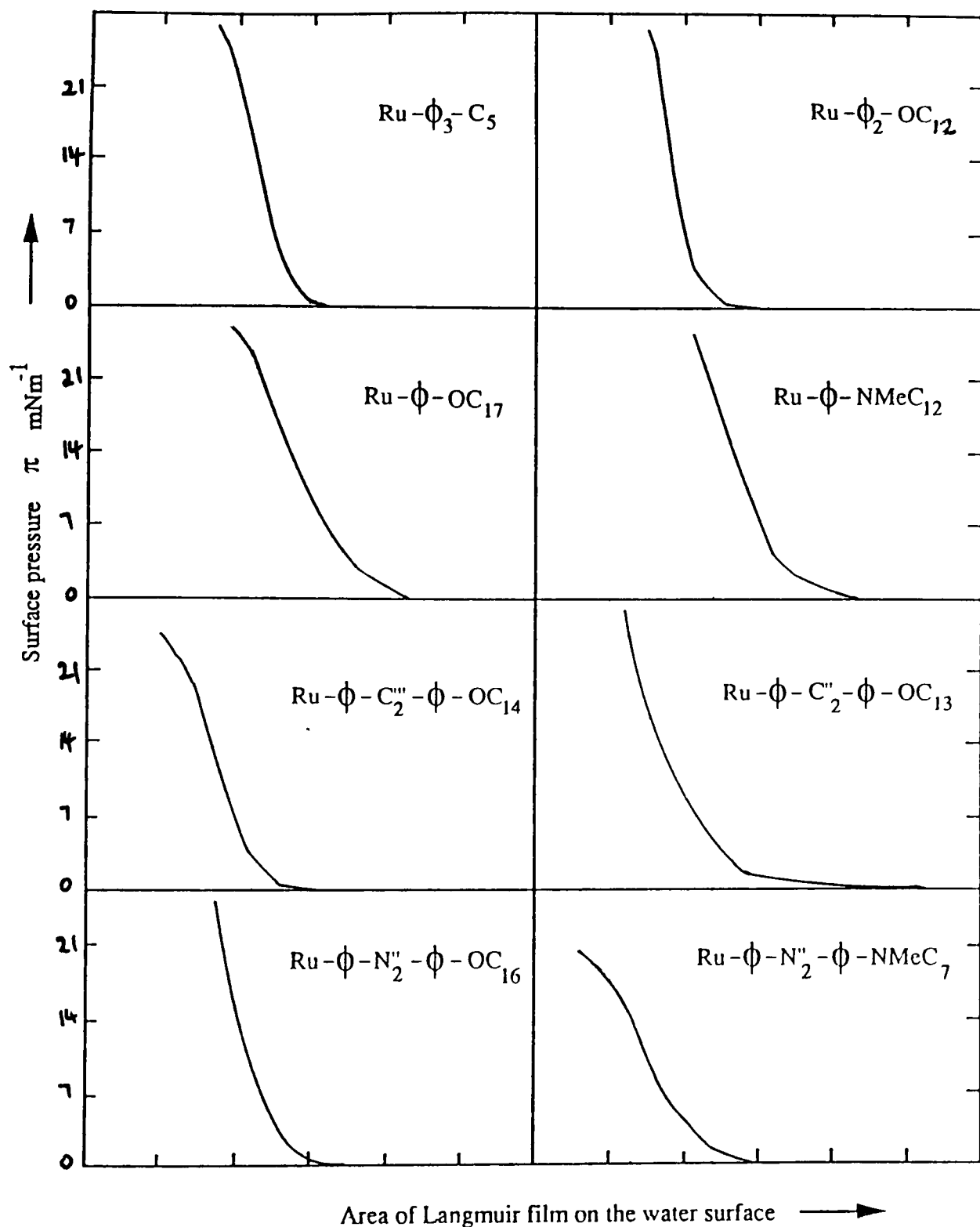


Figure 5.6 : Surface pressure - area isotherms for several organo-ruthenium complexes.

subtle phase transition in which the orientation of the molecules within the layer alter or a more drastic collapse mechanism whereby the surface pressure is so large that crystallisation from the layer commences. The loosely termed collapse pressure, π_c , occurs at 24.0 mNm⁻¹ for Ru- ϕ_3 -C₅ at this particular pH of 5.8 (π_c is defined as the pressure at which the collapse or re-ordering mechanism begins to act).

The solid region of the isotherm is relatively steep, although not as inclined as in the case of fatty acid Langmuir monolayers. The steepness of the gradient may be easily quantified by calculating the compressibility of the film which can be defined as:

$$k_s = \frac{-1}{A} \left(\frac{\delta A}{\delta \pi} \right) \quad (5.1)$$

where k_s is the compressibility, A is the area occupied by one molecule and π is the surface pressure. The quantity k_s therefore represents the fractional change in the area per molecule per mNm⁻¹ rise in surface pressure. For Ru- ϕ_3 -C₅ the value of k_s is 0.0117 mN⁻¹ compared with behenic acid whose compressibility is 0.0006 mN⁻¹ at pH 5.8. It is not surprising that the compressibility of the organo-ruthenium complex is far larger than that of a fatty acid material as the long axis of the ruthenium complexes are not close packed as in the case of the long hydrocarbon chains of behenic acid, and there is substantial opportunity for the triphenylphosphine ligands of adjacent ruthenium headgroups to intermingle. Such a process would, however, occur gradually and, of course, lead to a larger value of compressibility. Finally, it is interesting to note the pressure at which the most steeply rising region of the isotherm commences. This point marks the end of a quasi-liquid phase and the beginning of the solid-like phase in which the compressibility is minimised. For the example Ru- ϕ_3 -C₅, this transition pressure, π_{ls} , occurs at 7.0 mNm⁻¹. It is clear therefore that the structure of the surface pressure - area isotherm may be characterised by the parameters discussed above. The values of π_{ls} , π_c ,

k_s , and a_m , the area occupied by a single molecule, enable Langmuir films of different materials to be compared and contrasted.

The isotherms in Figure 5.6 represent a selection of the compounds that have been studied. A detailed account of the properties of each serves no purpose, although the predominant features of all the complexes investigated have been summarised in Table 5.2. This data will be commented upon at the end of this section.

Having discussed the predominant properties of the shape of the isotherms, it is appropriate to consider their use in the verification that the floating layer is indeed monomolecular. The number of molecules spread onto the water surface, N_T , is accurately known so that a simple division of the total area occupied by the layer by N_T yields an estimate of the area filled by a single molecule. The measured area can be compared with the expected value obtained using molecular modelling techniques. If the two areas are equal (within experimental error) then the floating layer must be only a single molecule thick.

Figure 5.7a shows an isotherm for complex $\text{Ru-}\phi_3\text{-C}_5$ using a spreading solvent concentration of 0.1 mgml^{-1} . It is clear that at a surface pressure of 20 mNm^{-1} , the measured area per $\text{Ru-}\phi_3\text{-C}_5$ molecule is 1.27 nm^2 . Computer-generated molecular modelling enables the physical dimensions of the complex to be estimated. This is in excellent agreement with the measured value from the isotherm especially if consideration is given to the possibility of interleaving of the triphenylphosphine ligands of adjacent ruthenium headgroups. These data are consistent with the organo-metallic headgroup resting on the water with the terphenyl groups and substituted alkyl chain protruding roughly normal to the surface as depicted in Figure 5.7b .

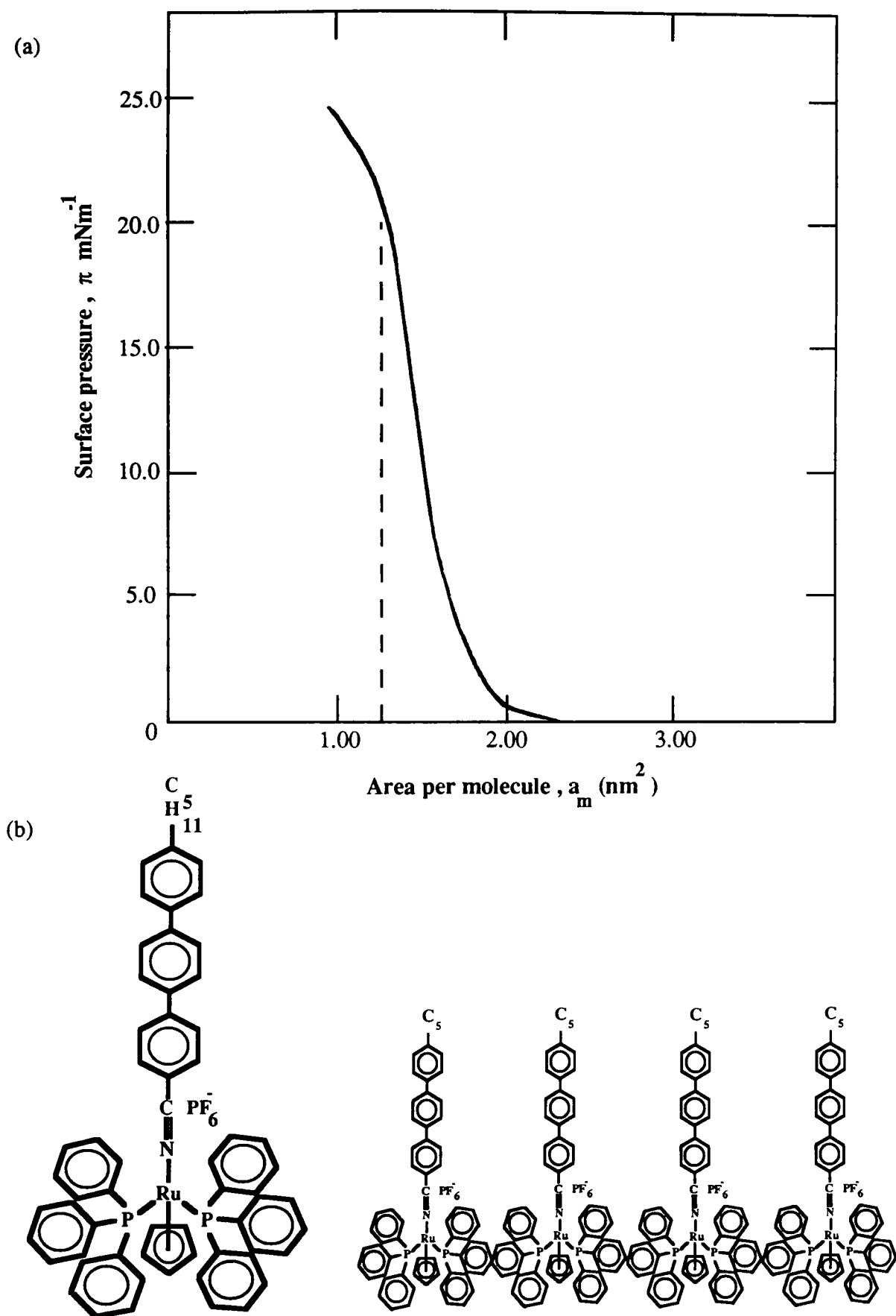


Figure 5.7 : (a) Surface pressure - area isotherm for Ru- ϕ -G monolayer and (b) the orientation of the molecules on the water surface.

The molecular area data therefore shows that the floating Langmuir film of Ru- ϕ_3 -C₅ is indeed monomolecular. Many of the *precursor* compounds studied in this work do not form stable Langmuir films owing to high solubility in the subphase or extremely low collapse pressures, but it has been shown that the complexation of a ruthenium (η^5 -cyclopentadienyl)-(bis triphenylphosphine) hexafluorophosphate group to the nitrile group of the precursor enables a stable floating layer to be studied.

Table 5.2 shows the characteristics of the isotherms of all the novel complexes investigated. There are several interesting and useful features shown by these data. Firstly, it is important to note that the majority of complexes exhibit area per molecule values in the range $1.15 < a_m < 1.45 \text{ nm}^2$ which is consistent with the values predicted from molecular modelling techniques. Often, a longer substituted alkyl chain leads to an increased molecular area. For example, in the series Ru- ϕ -OC_n, substitution of a pentyl or longer chain enables the area to rise into the above range. This effect is probably due to solubility in the water subphase. That is, complexes Ru- ϕ -OC₁ and Ru- ϕ -OC₃ are expected to be slightly soluble in water relative to the pentyl, dodecyl and heptadecyl derivatives. In addition, the molecular area may be influenced by the magnitude of the ground state dipole moment of the active long axis of the molecules or, more correctly, that of the dipole-dipole repulsion forces acting between adjacent molecules.

The collapse pressure also appears to be dependent upon the length of the carbon chain. Compounds Ru- ϕ -OC₁, Ru- ϕ -OC₅ and Ru- ϕ -N₂"- ϕ -NMeC₇ have lower π_c values than the longer Ru- ϕ -N₂"- ϕ -OC₁₆ and Ru- ϕ -C₂"- ϕ -OC₁₃. In the case of fatty acids, such a trend is also observed, and explained by the increased van der Waals' attractions along adjacent hydrocarbon chains. For the ruthenium complexes the triphenylphosphine groups of adjacent headgroups somewhat shield the active dipolar groups, such as the terphenyl chains of Ru- ϕ_3 -C₅, from close interaction, and therefore one would expect the collapse

Table 5.2: Langmuir film characteristics for organo-ruthenium complexes.

Ruthenium Complex	pH	π_{ls} mNm^{-1}	π_c mNm^{-1}	ζ_s mN^{-1}	a_m nm^2
$\text{Ru} - \phi_3 - \text{C}_5$	5.8	7.0	24.5	0.0117	1.27
$\text{Ru} - \phi_2 - \text{OC}_{12}$	5.9	10.0	27.0	0.0009	1.20
$\text{Ru} - \phi - \text{C}_{12}$	5.7	8.0	20.5	0.0153	1.18
$\text{Ru} - \phi - \text{OC}_1$	5.8	20.0	γ	γ	0.40^α
$\text{Ru} - \phi - \text{OC}_3$	5.8				
$\text{Ru} - \phi - \text{OC}_5$	5.8	7.0	16.0	0.0218	1.44^β
$\text{Ru} - \phi - \text{OC}_{12}$	5.9	12.5	21.5	0.0240	1.43
$\text{Ru} - \phi - \text{OC}_{17}$	6.0	4.0	24.5	0.0148	1.25
$\text{Ru} - \phi - \text{NH}_2$	5.9	19.0	28.0	0.0128	0.45^δ
$\text{Ru} - \phi - \text{N Me C}_{12}$	5.8	5.0	28.0	0.0130	1.04
$\text{Ru} - \phi - \text{C}_2''' - \phi - \text{OC}_{14}$	5.7	8.0	21.0	0.0266	1.31
$\text{Ru} - \phi - \text{C}_2'' - \phi - \text{OC}_{13}$	5.9	15.0	30.0	0.0006	1.19
$\text{Ru} - \phi - \text{N}_2'' - \phi - \text{OH}$	5.8	η			
$\text{Ru} - \phi - \text{N}_2'' - \phi - \text{OC}_{16}$	5.8	12.7	25.0	0.0119	1.18
$\text{Ru} - \phi - \text{N}_2'' - \phi - \text{NMe}_2$	5.8	η			
$\text{Ru} - \phi - \text{N}_2'' - \phi - \text{NMeC}_7$	5.9	8.4	16.5	0.0198	1.28^ϵ
$\text{Ru} - \text{C}_{18}$	5.8	–	–	–	0.92

α 25.0 mNm^{-1}

β 16.0 mNm^{-1}

δ 25.0 mNm^{-1}

ϵ 16.5 mNm^{-1}

γ Very expanded isotherm

η Collapsed immediately

behaviour to be governed by the characteristics of the interacting headgroups themselves. Most of the π_c values lie in the range $20 < \pi_c < 30 \text{ mNm}^{-1}$ which suggests that the collapse mechanism is complicated by other contributing factors in addition to the Ru-Ru interaction.

Finally, the compressibility of the complexes is difficult to analyse because the solubility of each complex is dependent on its pH. It will be seen later that LB deposition is most efficient for the majority of the compounds in the range $5.6 < \text{pH} < 6.0$ and so values for k_s in this range are given. However, the most noteworthy point is that the relatively large compressibilities exhibited by the organo-metallic complexes compared to fatty acids lead to very low rigidity of the Langmuir monolayers. Sometimes, even fatty acids can become extremely rigid on the water surface which can lead to localised high pressure regions and eventual collapse. This is because the Wilhelmy plate senses only the surface pressure in the region directly around the sensor itself which may not be representative of the surface pressure within the entire monolayer if the layer is rigid. No such problems are experienced with the ruthenium complexes.

The preparation of Langmuir layers of novel organo-ruthenium complexes has been described in detail in this section. The characteristics of the surface pressure area isotherms have shown that many of the materials possess the qualities required in order to be of use in the deposition process itself.

5.4.3 The dependence of surface pressure isotherms on pH.

The Langmuir film properties of many materials have been found to depend upon the hydrogen ion concentration of the subphase. Often, a "window" of pH values exists in which the molecular area of the compound is the expected value and the solubility and

areal stability of the monolayer are optimised. Behenic acid, for example, behaves optimally in the range $5.2 < \pi < 5.9$.

The isotherms of the novel ruthenium compounds depend on pH in a similar manner. Table 5.3 shows the values of a_m and π_c for $3.9 < \text{pH} < 8.7$ for two complexes Ru- ϕ_3 -C₅ and Ru- ϕ_2 -OC₁₂. For Ru- ϕ_3 -C₅, it is clear that in the range $4.6 < \text{pH} < 6.7$, the molecular area agrees accurately with the modelled value of 1.21 nm² and therefore it can be assumed that, over this pH range, the molecules are orientated with the ruthenium headgroups on the water surface and the alkyl substituted benzene rings protruding orthogonally. However, within this smaller pH range, the surface pressure may be increased to 24.5 mNm⁻¹ at pH 5.8 . It is logical therefore to use this pH as the molecules are most densely packed and ordered. Similarly, the collapse pressure for a monolayer of Ru- ϕ_2 -OC₁₂ is 27 mNm⁻¹ at pH 5.9 . This pH is coincidentally extremely convenient to use as pure water, initially at pH 7.0, naturally absorbs CO₂ gas, present in the air, and stabilises at around pH 5.8 . Therefore no acid or alkali must be added to the subphase to acquire the optimum pH.

5.4.4 The effect of concentration of the spreading solution on the Langmuir film properties.

It was mentioned previously in section 5.4.1 that the properties of the floating monolayers of the organo-ruthenium complexes are somewhat influenced by the concentration of the spreading solution. As an example, Figure 5.8 shows the measured normalised area per molecule of complexes Ru- ϕ -C₁₂ and Ru- ϕ -OC₅ as a function of the concentration of the solution. It is clear that for dilute solutions the molecular area is stable, but as the concentration increases, the area begins to decrease rapidly. For the complexes investigated, it has been found that at mass concentrations $< 0.15 \text{ mgml}^{-1}$, the molecular area measured from the isotherm agree most accurately with the modelled value.

Table 5.3 : Optimisation of subphase pH for organo-ruthenium Langmuir films.

Ruthenium Complex	pH	π_c mNm^{-1}	a_m nm^2
$\text{Ru}-\phi_3-\text{C}_5$	3.9	14.0	1.59
$\text{Ru}-\phi_3-\text{C}_5$	4.6	15.0	1.31
$\text{Ru}-\phi_3-\text{C}_5$	5.8	24.5	1.27
$\text{Ru}-\phi_3-\text{C}_5$	6.7	20.0	1.29
$\text{Ru}-\phi_3-\text{C}_5$	8.7	21.0	1.06
$\text{Ru}-\phi_2-\text{OC}_{12}$	4.6	21.5	1.19
$\text{Ru}-\phi_2-\text{OC}_{12}$	5.9	27.0	1.20
$\text{Ru}-\phi_2-\text{OC}_{12}$	8.0	20.7	1.09

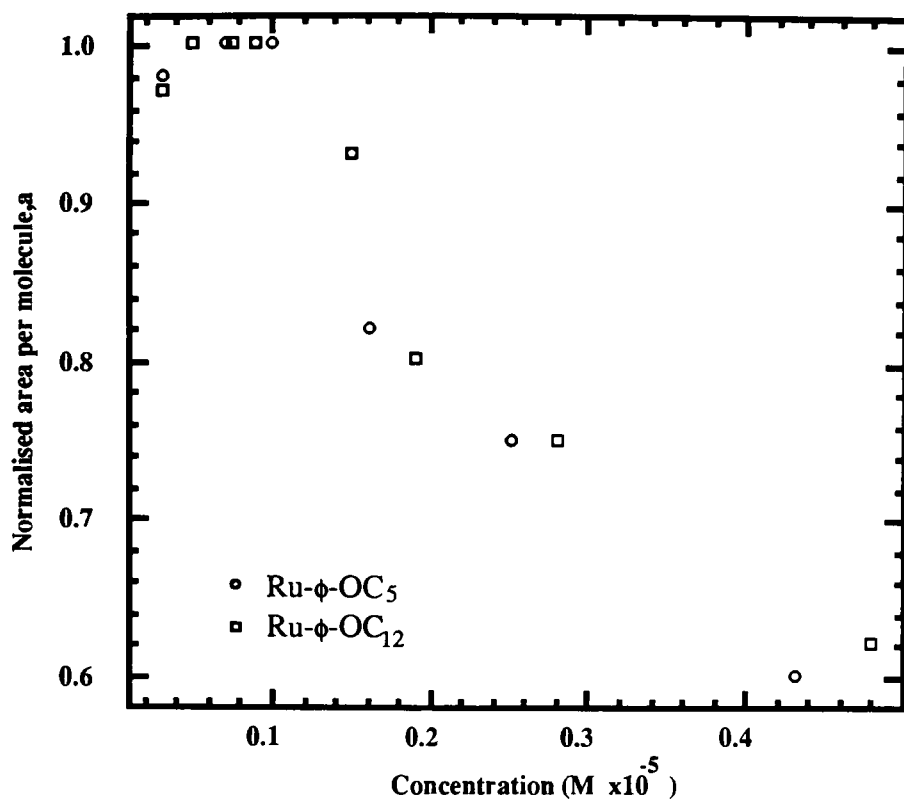


Figure 5.8 : The concentration dependence of the molecular area of the ruthenium complexes Ru-φ-OC₅ and Ru-φ-OC₁₂ .

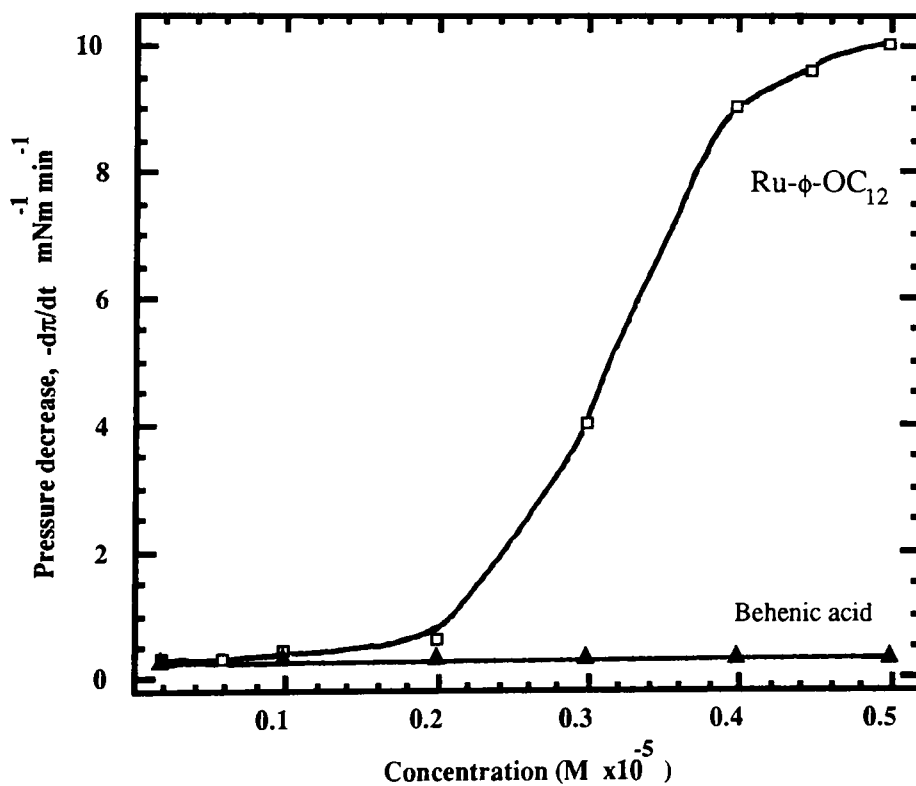


Figure 5.9 : Rate of pressure decrease as a function of concentration for behenic acid and a ruthenium complex.

The explanation for the observed concentration effect probably rests upon the efficiency and completeness with which the distribution of the solute molecules is implemented by the spreading solvent. Unlike fatty acid molecules which disperse spontaneously over the water surface, the ruthenium molecules do not possess a *strongly* hydrophilic headgroup and will therefore not spread readily. It is sensible to assume that improved distribution occurs when the volume of spreading solvent per unit mass of solute is increased. Clearly, a cut-off or saturation limit is observed at which point highly efficient spreading occurs. When the volume of solvent per unit mass of ruthenium complex decreases (concentration increases) the solvent can no longer cope with dispersing the solute successfully. This leads to regions where the molecules have coagulated and disrupt the ordered monolayer structure. Figure 5.9 provides further evidence for this hypothesis. The surface pressure within the monolayer may be increased to just below the onset of collapse (20 mNm^{-1}) when the *area* is maintained at a constant value and the reduction in surface pressure is monitored as a function of time. Behenic acid shows only a very small fall in pressure per unit time which is independent of concentration although the relationship is dramatic for the organo-metallic compounds. Indeed, the pressure decrease becomes progressively more pronounced as the concentration increases. This is due to the presence of localised regions of unspread bulk material which act as nucleation sites for further collapse. At low concentration ($< 0.15 \text{ mNm}^{-1}$), however, the film is entirely monomolecular and the rate of pressure decrease occurs mainly due to molecular re-ordering and slight solubility in the subphase.

5.4.5 The areal stability of organo-ruthenium Langmuir films.

In Chapter 2, the importance of maintaining a constant surface pressure during deposition of a floating monolayer was stressed. It is also advantageous if the area occupied by the Langmuir film under constant compression (but not undergoing deposition) remains as

stable as possible. Area losses may be accounted for by solubility in the subphase, molecular re-ordering and collapse. Behenic acid, for instance, is extremely stable on the water surface and suffers an area loss of typically only 0.1 % hr⁻¹. Most other compounds, however, including the organo-ruthenium salts, display lower stability although usually acceptable levels are encountered. Again, this parameter is dependent on the spreading solution concentration: that is, the monolayer area is more stable as the concentration decreases owing to the reduction in the number of nucleation centres for crystallisation from the monolayer.

5.4.6 Characterisation of monolayer compression using uv-visible spectroscopy.

The reduction in area available to a floating Langmuir monolayer causes the molecules to approach each other more closely so that intermolecular forces such as van der Waals' and dipole-dipole interactions become significant. These are often exposed using spectroscopic techniques as the molecular energy levels are perturbed as a result thus modifying the electronic absorption transitions. However, the optical absorption of the floating monolayer is very weak and accordingly the spectrophotometer used must be extremely sensitive in order to detect changes that occur during the compression.

The Otsuka Electronics MCPD-100 3C instrument available in the Oxford Molecular Electronics Laboratory has been used extensively to study the floating monomolecular layers of organo-ruthenium complexes. Figure 5.10 shows the optical absorption spectra as a function of surface pressure for the complexes Ru- ϕ -C₂"- ϕ -OC₁₃ and Ru- ϕ -N₂"- ϕ -NMeC₇ using the uv-emitting deuterium source (250 - 500nm) and the tungsten visible source (400 - 1000nm) respectively. It is clear that as the surface pressure begins to rise, the optical absorbance of Ru- ϕ -C₂"- ϕ -OC₁₃ monolayer increases dramatically as expected. The absorption continues to increase provided the molecules are

approaching each other more closely. When the monolayer begins to resist further compression, however, the absorption saturates because the number of absorbers per unit area remains roughly constant. Another subtle change in the absorbance spectra of the floating monolayers concerns the position of the wavelength of maximum absorption, λ_{max}^L . Although small, this effect can be seen in Figure 5.10b where the peak absorbance at low surface pressure (0.1 mNm^{-1}) occurs at 359nm but gradually shifts to the lower wavelength of 356nm at high pressure (15 mNm^{-1}). This shift is only slightly greater than twice the resolution of the spectrophotometer (1.0nm) so that it is by no means conclusive. It must be noted, however, that even at 0.1 mNm^{-1} , the molecules are extremely close together (average separation is about 0.5 nm) compared to the solution (average separation roughly equal to 30nm) and consequently the dipole-dipole interactions are proportionally larger.

Reference to Figure 5.10a clearly depicts the larger shift in λ_{max}^L that occurs for a monolayer of $\text{Ru-}\phi\text{-N}_2^{\text{''}}\text{-}\phi\text{-NMeC}_7$. The value at low pressure is 500nm and gradually reduces to 480nm during compression as the molecules become more aligned and ordered. The lowest energy transitions in the solutions of $\text{Ru-}\phi\text{-C}_2^{\text{''}}\text{-}\phi\text{-OC}_{13}$ and $\text{Ru-}\phi\text{-N}_2^{\text{''}}\text{-}\phi\text{-NMeC}_7$ occur at 368nm and 498nm respectively. In both cases the high pressure values of λ_{max}^L is much lower (12nm and 18nm respectively) than the solution values indicating that the energy of the transition in the Langmuir film is higher than that of the free molecule in solution. This has often been found to occur when parallel aligned dipoles begin to mutually interact. In addition, the shift is larger for $\text{Ru-}\phi\text{-N}_2^{\text{''}}\text{-}\phi\text{-NMeC}_7$ than for $\text{Ru-}\phi\text{-C}_2^{\text{''}}\text{-}\phi\text{-OC}_{13}$ which is consistent with the higher ground state dipole moment of the $\text{Ru-}\phi\text{-N}_2^{\text{''}}\text{-}\phi\text{-NMeC}_7$ complex. The dipole-dipole repulsion is stronger as the dipole moment increases. Table 6.2 lists the lowest energy transitions for the Langmuir films of several ruthenium complexes compared to their values in solution (chloroform).

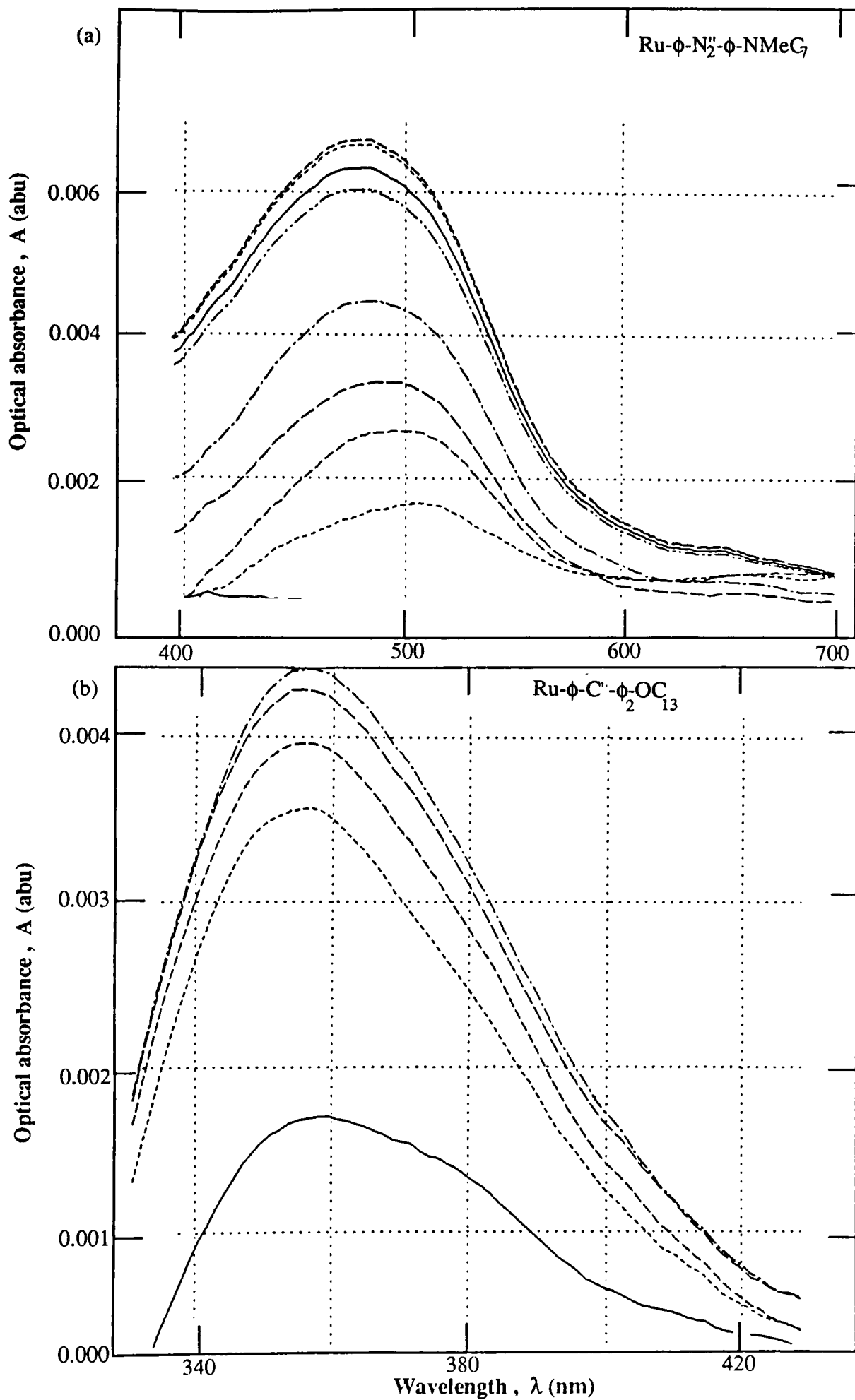


Figure 5.10 : Monitoring the compression of monolayers using the spectrophotometer.

5.5 Heterogeneous Langmuir film studies.

It is occasionally necessary to mix the organo-ruthenium molecules of interest with those of a carboxylic acid or other material to form a mixed spreading solution in order to improve the areal stability of the resultant Langmuir monolayer. In addition, such investigations can yield useful information regarding the molecular packing within the film. In this work, two types of mixed layer systems have been assessed. Firstly, the behaviour of several of the ruthenium complexes in a behenic acid matrix has enabled the optimum composition ratio of the components to be determined for deposition purposes. Secondly, a novel system in which the ruthenium complex is mixed with its corresponding precursor compound has allowed the large voids between the molecular tails to be filled thus increasing the packing density of active dipoles on the water surface and consequently in the transferred layer.

5.5.1 The ruthenium complex : behenic acid system.

It has been discussed previously that the area occupied by a single ruthenium molecule is typically around 1.20 nm^2 in the homogeneous Langmuir layer. Such an area is assumed to correspond to reasonably efficient packing of the ruthenium headgroups as was pictorially represented in Figure 5.7b . However, when the complexes are held in a fatty acid matrix, the efficiency with which all the molecules pack together in the two-dimensional floating lattice is found to be dependent upon the molar fraction of each component material. The number of molecules of each material per unit volume of solvent in the spreading solution is accurately known so that it is straightforward to calculate the average area per molecule from the π - A isotherm. Figure 5.11a shows the average area per molecule as a function of the molar fraction indicating that, indeed, the efficiency of packing deteriorates for a molar fraction > 0.3 for $\text{Ru}-\phi-\text{C}_2''-\phi-\text{OC}_{14}$ and > 0.45 for Ru-

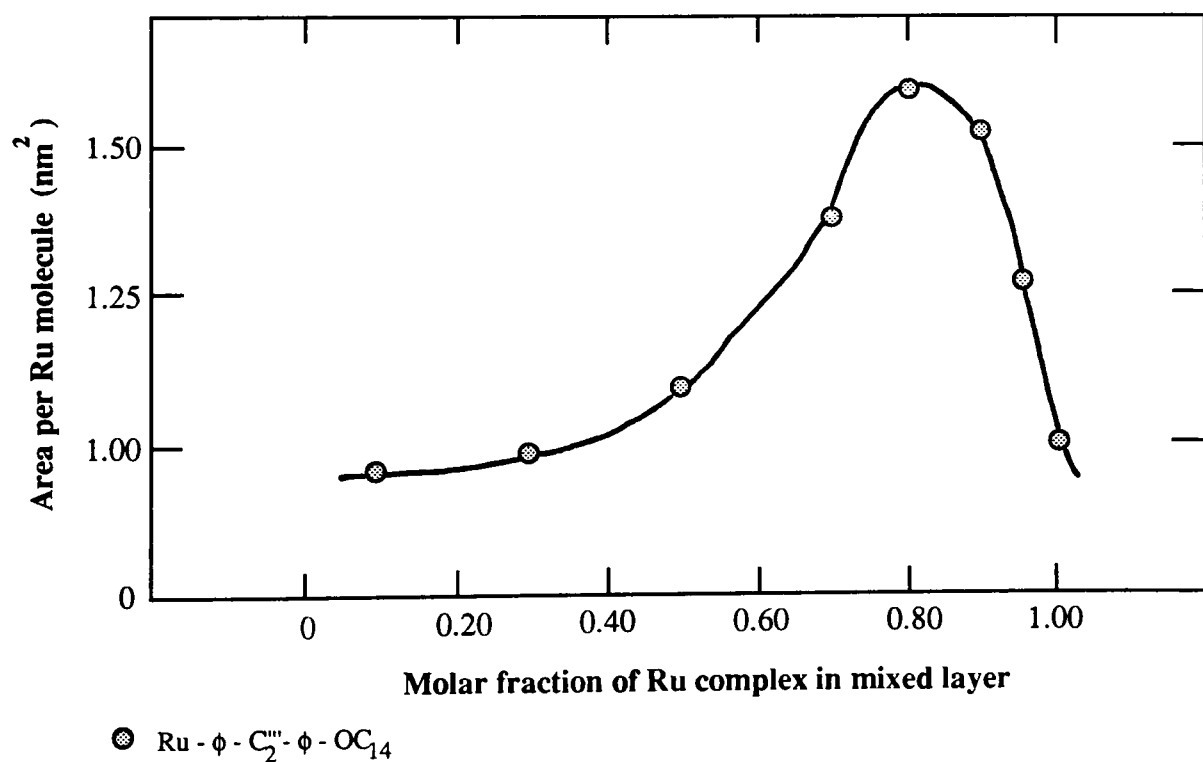
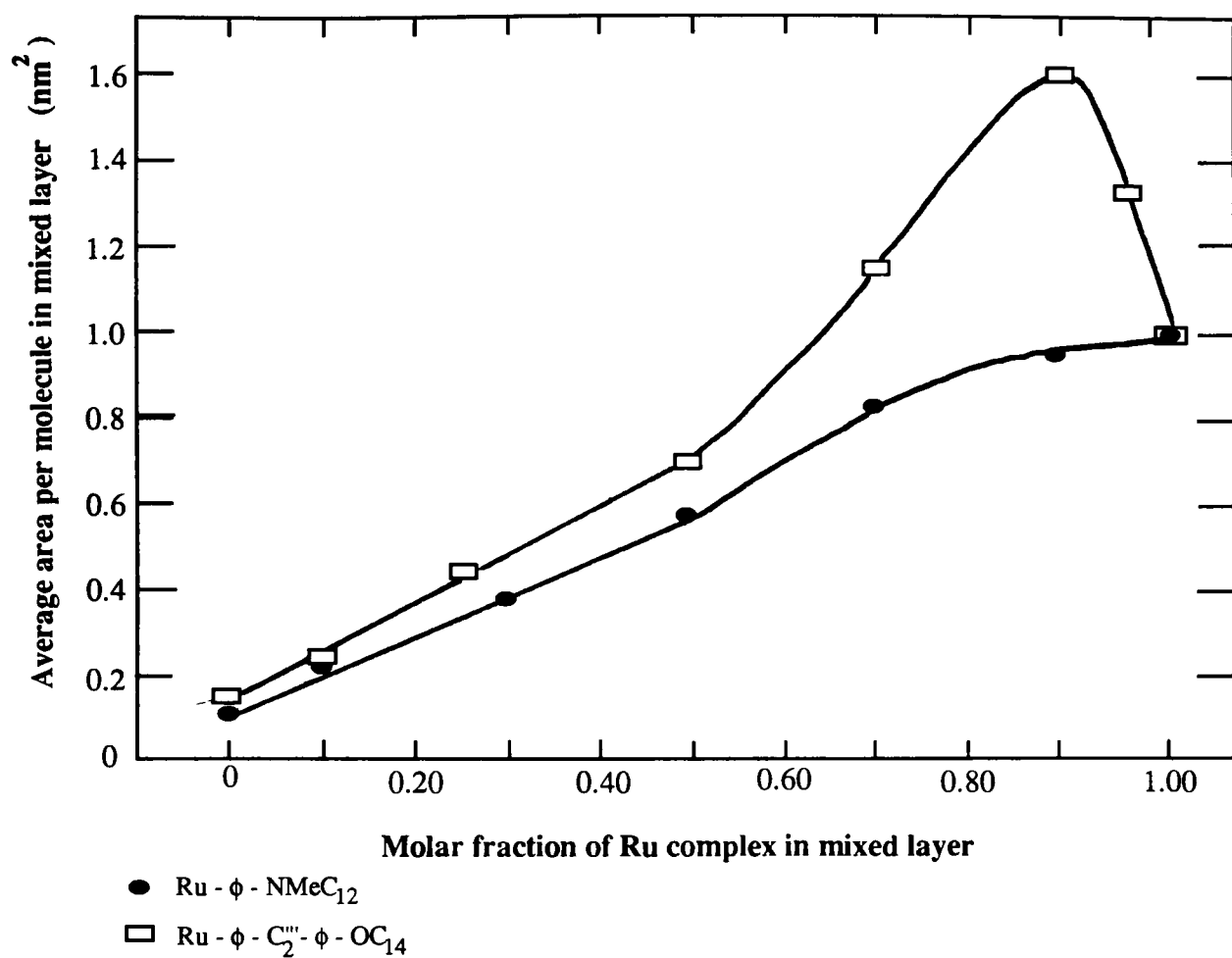


Figure 5.11 : Mixed layer Langmuir film studies. (a) Average area per molecule in mixed system and (b) variation in the area per Ru molecule in the mixed system.

ϕ -NMeC₁₂. It must be stressed that a constant concentration for all mixed solutions was used such that the spreading efficiency was kept constant. The area occupied per ruthenium molecule is calculable if that taken up by each behenic acid molecule is itself assumed to be 0.21 nm² (the value obtained from the isotherm of the homogeneous behenic acid monolayer). The expression below holds for miscible component materials:

$$A N_T = N_B A_B + N_{Ru} A_{Ru} \quad (5.2)$$

where N_T = the total number of molecules (of both types) in the mixed layer, A = the mean area per molecule, $N_{B,(Ru)}$ = the number of molecules of behenic acid (ruthenium complex) and $A_{B,(Ru)}$ = the area per molecule of each component. If the above assumption is made, the calculated value of A_{Ru} takes into account the intermolecular spaces on the water surface not filled by molecules in addition to its own molecular cross-sectional area. Thus the variation in A_{Ru} as a function of molar composition exposes any change in molecular arrangement that occurs. Figure 5.11b shows the plot of A_{Ru} versus the molar fraction of the complex Ru- ϕ -C₂₂- ϕ -OC₁₄. The increase in value of A_{Ru} suggests that the bulky ruthenium molecules begin to disrupt the packing of the acid molecules above the molar ratio of 0.3. It is noticeable that the maximum disruption occurs at the 0.8 : 0.2 ruthenium:behenic acid mixture which is surprising on consideration of the difference in cross-sectional areas of each component (0.2 nm² and 1.2 nm² respectively).

Clearly, the most compact mixed layer films are found when the ruthenium molar fraction, M_{Ru} , is in the range $0 < M_{Ru} < 0.3$ for Ru- ϕ -C₂₂- ϕ -OC₁₄ and $0 < M_{Ru} < 0.45$ for Ru- ϕ -NMeC₁₄. These molar fractions will lead to the highest surface density of dipolar molecules *in the mixed system*.

5.5.2 Molecular incorporation of precursors into the organo-ruthenium lattice.

The molecular areas of the organo-ruthenium complexes described in this thesis are relatively large (1.2 nm²) when compared with those of fatty acid molecules (0.2 - 0.3 nm²). Therefore, the resulting surface molecular density of the floating or transferred films is relatively low which often leads to a reduced macroscopic second-order non-linear effect such as optical second-harmonic generation and pyroelectricity. It has been found possible, however, to increase the packing density by impregnating the close-packed organo-ruthenium lattice with molecules of the corresponding precursor compound. A detailed investigation of the isotherms of various mixtures of Ru- ϕ_3 -C₅ and NC- ϕ_3 -C₅ supported the hypothesis that some of the NC- ϕ_3 -C₅ dopant molecules are indeed incorporated into the spaces between the terphenyl chains of adjacent Ru- ϕ_3 -C₅ molecules. The area occupied by molecules on the water surface which adopt this structure can be written:

$$\alpha = \frac{A_T}{N_{Ru}} = \frac{\{N_{Ru}A_{Ru} + A_P(N_P - KN_{Ru})\}}{N_{Ru}} \quad (5.3)$$

for $N_P \geq KN_{Ru}$ where α = a "defined" area equal to the ratio A_T/N_{Ru} , A_T = the total area occupied by the entire film, $N_{Ru,p}$ = the number of molecules spread of Ru- ϕ_3 -C₅ and NC- ϕ_3 -C₅ respectively, $A_{Ru,p}$ = the molecular area of each component molecule, and K = an "incorporation" factor which signifies the number of precursor molecules *within* the ruthenium lattice per Ru- ϕ_3 -C₅ molecule. This expression describes the contribution to the total area of the floating film made by each component. The curve (a) in Figure 5.12 is the theoretical curve expected if *no* incorporation occurs and *all* the molecules contribute to the film area. However, the experimental curve (b) shows that the area α (normalised to

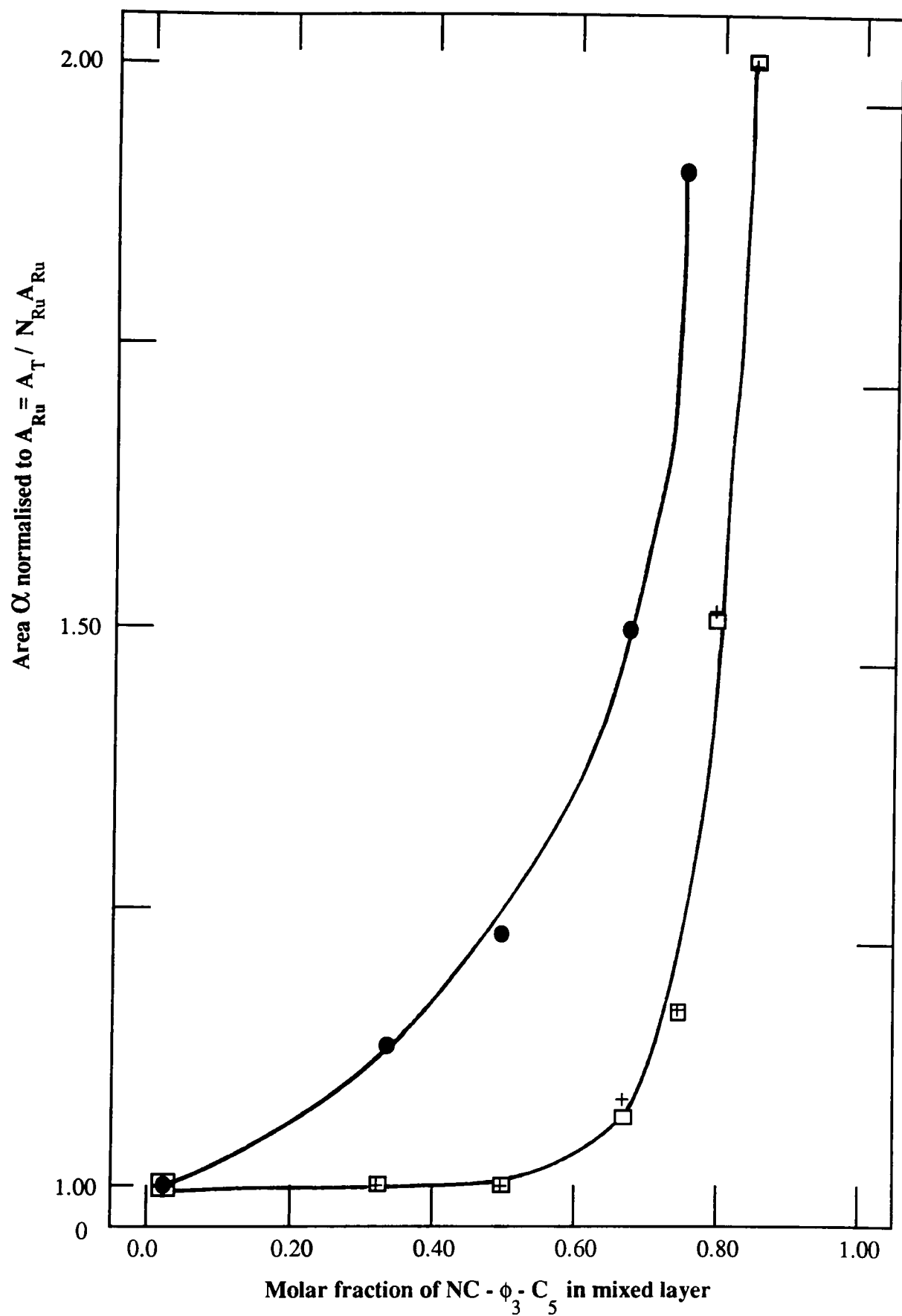


Figure 5.12 : Incorporation of NC - ϕ_3 - C_5 molecules into a floating layer of Ru - ϕ_3 - C_5 .
 $\bullet$ Theoretical response for zero incorporation, $\square$ Experimental curve,
 $+$ Theoretical curve for $K = 1.7$.

the area of the Ru molecules in a homogeneous layer: 1.2nm^2) remains constant until about 65 % of the layer is composed of the precursor molecules. Above this molar fraction, the value of α begins to rise. Curve fitting the experimental results to theoretical data from equation 5.3 shows that 1.7 precursor molecules per ruthenium molecule are incorporated into the ruthenium lattice. The vacant volume of space within the lattice would allow approximately 2.0 molecules to be incorporated if the packing were ideal.

It is apparent, therefore, that the precursor molecules do not contribute to the total film area until a critical molar fraction of 0.65 only above which they cause an increase in area occupied by the monolayer. This hypothesis is difficult to confirm although there are two additional reasons that support it. Firstly, the "incorporated" monolayer (transferred as an LB film) shows a 50 % improvement in second-harmonic signal strength and secondly, a piezoelectric quartz microbalance study revealed that a larger mass per unit area is transferred onto the transducer using the incorporated layer compared to the homogeneous Ru- ϕ_3 -C₅ layers. These results are discussed in Chapter 6.

5.6 Summary.

In this chapter, the details of the preparation and characterisation of Langmuir monolayers of a novel series of organo-ruthenium complexes have been presented. The study of their uv-visible spectroscopy has enabled the relationship between the optical absorption and the molecular structure to be studied which has relevance to the synthesis and the non-linear optical characterisation using the EFISHG technique. The organo-metallic complexation reaction has been shown to lead to a group of materials which form high quality floating monomolecular films on the surface of water. Their surface pressure - area isotherms have been rigourously investigated and explained in terms of their intricate molecular structure. The highly sensitive MCPD spectrophotometer has been used to

monitor the compression of monolayers and the importance of mixed layers has been mentioned with respect to producing improved quality floating layers and subsequently enable more efficient transfer onto a solid substrate to occur.

CHAPTER 6

Characterisation of LB Films of Novel Organo-Ruthenium Complexes.

6.1 Introduction.

In this chapter, the characteristics of the Langmuir-Blodgett (LB) films of organo-ruthenium complexes will be discussed in relation to their optical, structural, electrical and thermal properties. The optimum deposition conditions are shown for reference although the optimisation process is described only briefly. It must be stressed, however, that a great deal of laborious research effort was required initially to develop the organo-metallic headgroup that has enabled this novel class of materials to be designed, and, further to this, to optimise the transfer conditions. .

The optical characterisation of the materials under investigation has been presented in section 6.3 . The uv-visible spectrophotometer has been used extensively to assess the reproducibility of the deposition of successive monolayers onto a substrate. The position of the maximum absorption wavelength of the LB films has been compared to that of the floating Langmuir film and the spreading solution in order to relate the spectral characteristics to the molecular organisation within the medium. It is also interesting to observe the spectral changes that occur when the complex is mixed with a fatty acid or the

corresponding precursor. Consideration should be given to optical interference effects when measuring the absorbance of a sample because the reflectance properties change as a function of thickness. The interference characteristics of a mixed behenic acid : ruthenium complex LB film are therefore described in order to demonstrate this phenomenon. The other optical techniques that have been used for characterisation are ellipsometry and the surface plasmon resonance method [106], both of which have enabled accurate estimates of the refractive indices of several of the organo-ruthenium complexes to be measured with excellent mutual agreement. The non-linear optical properties of the complexes have been omitted from this chapter and included in Chapter 7 with the results of the EFISHG experiments.

Various techniques have aided the structural characterisation of the LB films and these are outlined in section 6.4 . They include transmission electron diffraction (TED), ESCA surface analysis, and scanning optical microscopy (SOM). Each technique has provided useful information concerning the structure and composition of the LB films, although a more thorough structural investigation is currently in progress using X-ray diffraction, reflection high energy electron diffraction (RHEED) and infra-red spectroscopy in addition to the techniques mentioned above.

Section 6.4 concerns the electrical measurements that have also been performed. The quartz microbalance has been found to be an excellent research tool to establish the reproducibility of the deposition process. Its extreme sensitivity coupled to the ease with which the piezoelectric quartz oscillators may be coated allow the deposition of a material to be characterised quickly and accurately. The MIM capacitance of several organo-metallic complexes and corresponding heterogeneous LB layers has been measured in order to yield information regarding the dielectric thickness (d/ϵ_r). An attempt has been made unsuccessfully to measure the lateral electrical conductivity of the complexes.

Finally, the thermal properties of this class of compounds have been assessed. The complexation of the ruthenium (η^5 -cyclopentadienyl)-(bis triphenylphosphine) hexafluorophosphate headgroup to the nitrile-terminated precursors effectively induces improved thermal stability [107]. The details of this effect have been described in section 6.5 in which the relationship between the bulk powder melting points and the molecular structure and packing properties are interrelated. The temperatures at which the LB films themselves thermally deteriorate have been studied. Such thermal stability data are important when considering the long-term practical use of organic materials in optical or pyroelectric devices. The pyroelectric response of the organo-ruthenium complexes has provided the major stimulus for further concurrent study in relation to thermal imaging applications. However, the pyroelectric data are presented in the Chapter 7 which concerns non-linear physical properties.

This chapter is concerned with the characterisation of LB films of the organo-ruthenium complexes, with particular emphasis placed upon the relationship between their macroscopic physical properties and the detailed molecular structure.

6.2 LB deposition of organo-ruthenium complexes.

This section details the transfer of the novel organo-metallic compounds developed for LB deposition. In particular, the optimisation process to establish the conditions required for reproducible deposition is discussed followed by a detailed account of their characterisation using many investigative techniques such as uv-visible spectroscopy, electron diffraction and ellipsometry. The pyroelectric response has been found to be relatively high in relation to other LB film materials. The non-linear optical response of the films will be discussed in the following chapter.

6.2.1 The optimum deposition conditions.

Many researchers in the field of LB deposition recognise the importance of optimising the conditions under which transfer of floating monolayers onto a solid substrate occurs. The Langmuir film characteristics often depend upon the pH of the subphase for instance. For deposition purposes, it is essential that the areal stability of the Langmuir layer on the water surface is optimised such that the structure of the molecules within the film remains constant. This form of stability may often be controlled by altering the pH of the subphase, although pH also has a dramatic effect upon the pressure at which monolayer collapse, π_c , initiates in monolayers of the ruthenium complexes. A compromise is therefore necessary between the three parameters pH, π_c and the areal stability, Σ_a . Figure 6.1a shows the relationship between π_c and pH for a Ru- ϕ_3 -C₅ floating monolayer while the dependence of Σ_a upon pH is shown in Figure 6.1b . Clearly, the optimum pH with respect to collapse pressure is 5.8 and that corresponding to areal stability is 4.6. A possible compromise would lead to the selection of pH 5.2 . However, care must be taken to reduce the acidity of the subphase owing to the possibility of chemical attack of the ruthenium complex and, a pH in the range 5.6 - 5.8 is used. This is a convenient value to employ as pure water at pH 7.0 gradually absorbs carbon dioxide from the ambient and equilibrates to about pH 5.7 . Therefore, it is not necessary to add acid or alkali solution to the subphase which reduces the preparation time of the monolayer before deposition significantly.

The deposition of the first floating Langmuir film is highly dependent upon the monolayer - substrate compatibility and the rigidity of the layer on the water surface. The speed at which transfer is possible is also often a determining factor in optimising the efficiency of deposition as shown in Figure 6.2 in which the deposition ratio is plotted as a function of speed for complex Ru- ϕ -OC₁₇. The optimum speed for this complex is 0.02 cm s⁻¹.

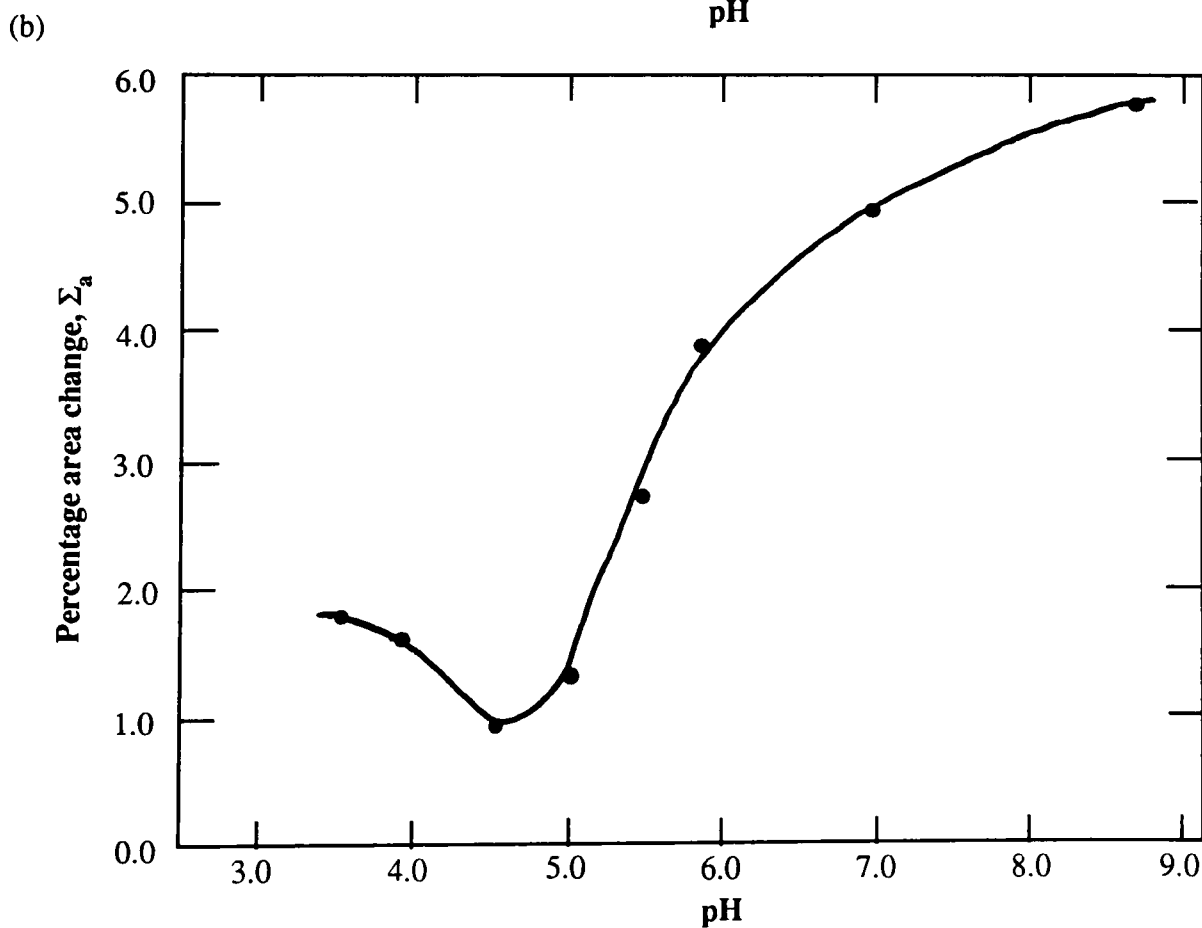
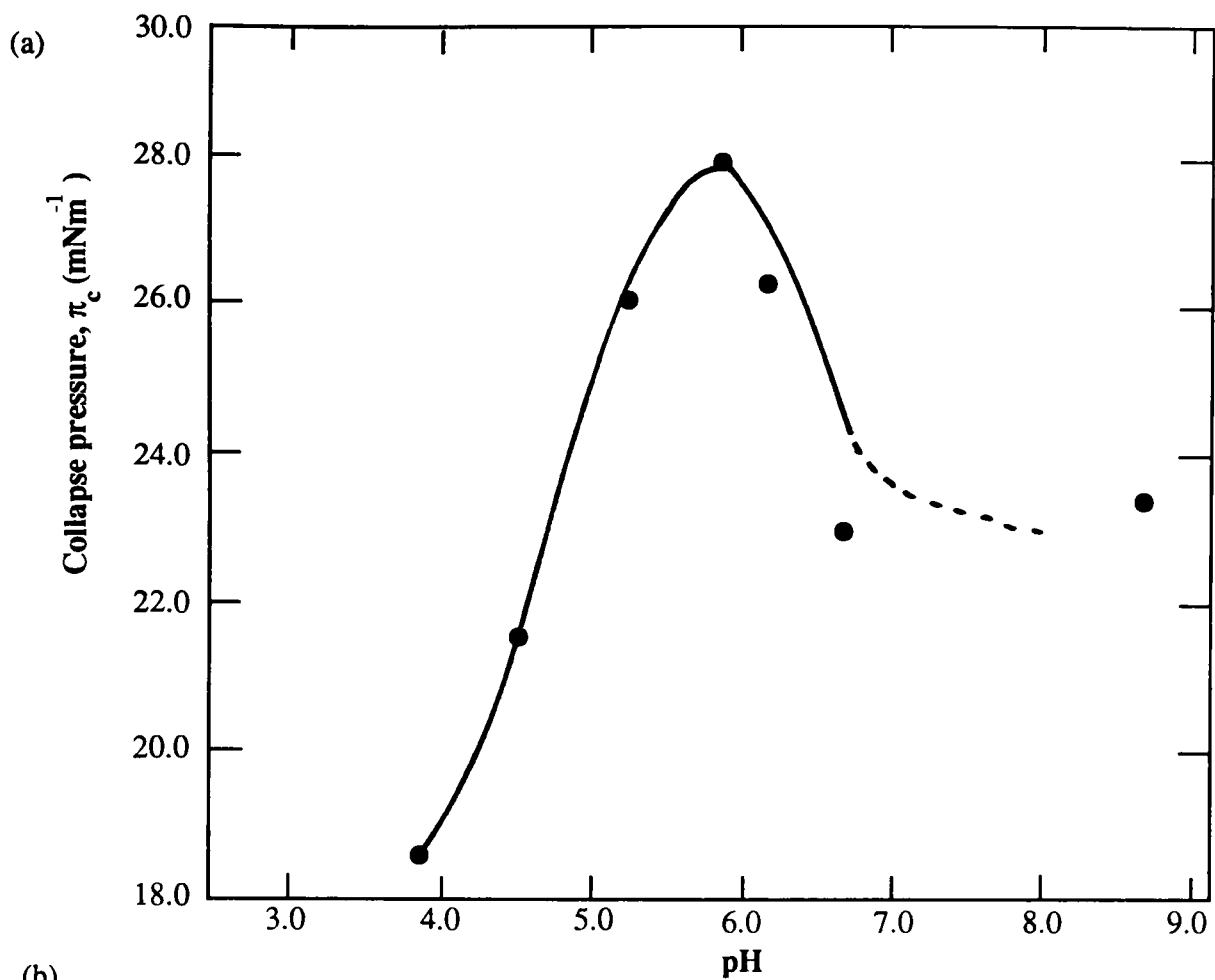


Figure 6.1 : Optimisation of deposition conditions for Ru- ϕ_3C_5 monolayers. (a) Surface pressure versus pH and (b) percentage area loss versus pH.

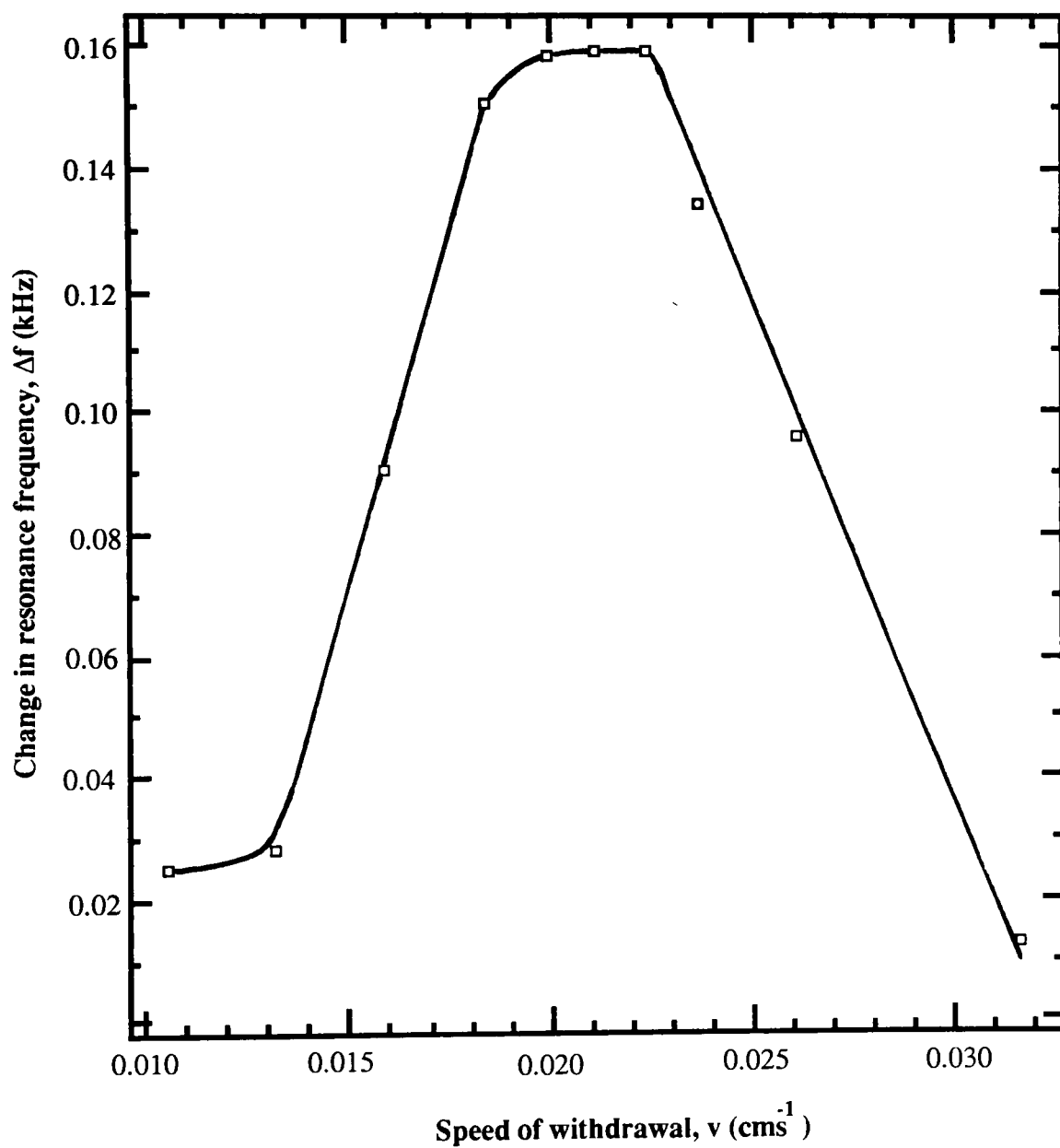


Figure 6.2 : The optimisation of the withdrawal speed for complex $\text{Ru-}\phi\text{-OC}_{17}$ monolayers.

Table 6.1 details the deposition conditions at which all the ruthenium complex monolayers are transferred. It is not surprising that the majority of the complexes may be best deposited using similar subphase conditions because the Langmuir film properties appear to be governed predominantly by the properties of the ruthenium headgroup itself.

6.2.2 Types of deposition.

In Chapter 2, the different configurations that monolayers may adopt in multilayer LB films were discussed. It was mentioned that the fatty acids invariably deposited in the Y-type manner in which transfer of the Langmuir film onto the substrate occurs both during the upward and downward transitions. The resulting macroscopic structure is centrosymmetric and, therefore, of no use in second-order physical applications. The alternative deposition modes using a single material are X or Z type.

The ruthenium complexes described in this work can all be transferred in the Z-type manner in which the surface pressure is reduced to zero or a very low value before each downstroke. However, some of the complexes transfer *only* as the substrate is raised through the floating layer *even* when a constant surface pressure is maintained at all times. In order to distinguish between these two types of Z-mode deposition, the latter will be termed Z*-type. A few of the complexes, however, transfer on the upstroke *and* on the downstroke but all are characterised by a slightly different behaviour to that of classical Y-type fatty acids; namely, the transfer ratio on each downstroke is always significantly less (<0.8) than that on each upstroke (>0.95) and shall be termed Y*-type deposition. It should be mentioned that none of the complexes can be deposited in the X-type mode.

The modes of deposition are shown for all the complexes in Table 6.1 . It can be seen that there is a tendency for the complexes possessing large ground state dipole

Ruthenium Complex	pH	Deposition pressure mNm⁻¹	Optimum speed cms⁻¹	Type of deposition
Ru-ϕ_3C₅	5.8	23.0	0.01	Z, Y*, A
Ru-ϕ_2OC₁₂	5.9	25.0	0.01	Z, Y*, A
Ru-ϕ-OC₅	5.8	15.0	0.025	Z, Y*, A
Ru-ϕ-OC₁₂	5.9	20.0	0.02	Z, Y*, A
Ru-ϕ-OC₁₇	6.0	23.0	0.02	Z, Y*, A
Ru-ϕ-NMeC₁₇	5.8	28.0	0.015	Z, Y*, A
Ru-ϕ-C₂^{'''}-ϕ-OC₁₄	5.7	20.0	0.01	Z*, A
Ru-ϕ-C₂^{''}-ϕ-OC₁₃	5.9	27.0	0.01	Z, Y*, A
Ru-ϕ-N₂^{''}-ϕ-OC₁₆	5.8	23.0	0.01	Z*, A
Ru-ϕ-N₂[']-ϕ-NMeC₇	5.9	15.0	0.01	Z*, A

Table 6.1 : The optimum deposition conditions for the organo-ruthenium complexes studied in this work.

moments to deposit in the Y*-type configuration. Such dipole-dipole interactions will favour the adoption of this thermodynamically more stable structure.

6.3 Optical characterisation of organo-ruthenium LB films.

In this section, the use of optical techniques for the assessment of transferred monolayer and multilayer LB films has been detailed. Uv-visible spectroscopy has been used to examine the spectral characteristics of the deposited films. The absorbance per monolayer, α_m , the wavelength of maximum absorbance of the LB film, $\lambda_{\text{max}}^{\text{LB}}$, and the wavelength shifts from the λ_{max} values of the floating layer and the solutions have been studied and explained in terms of the molecular arrangement within the monolayer and multilayer. In addition, ellipsometry and the surface plasmon resonance technique have yielded refractive index data and information regarding the uniformity of the film.

6.3.1 Uv-visible spectroscopy.

(i) Single material LB films.

The Beer-Lambert law predicts that the relationship between the optical absorbance and thickness of a thin homogeneous film should be linear. Therefore, such an investigation can be used to confirm the reproducibility of successive monolayer transfer. Figure 6.3 depicts such a study for Ru- ϕ -C₂'''- ϕ -OC₁₄ monolayers successively transferred onto a Corning 7059 glass substrate. The optical absorption was measured after the deposition of each bilayer such that the growth of the multilayer spectrum was monitored at regular stages throughout the process. Ru- ϕ -C₂'''- ϕ -OC₁₄ monolayers deposit unusually in the Y*-type configuration which may occur as a result of the large molecular ground state dipole moment. Figure 6.3a shows the absorbance as a function of wavelength, and Figure 6.3b plots the peak absorbance versus the number of monolayers

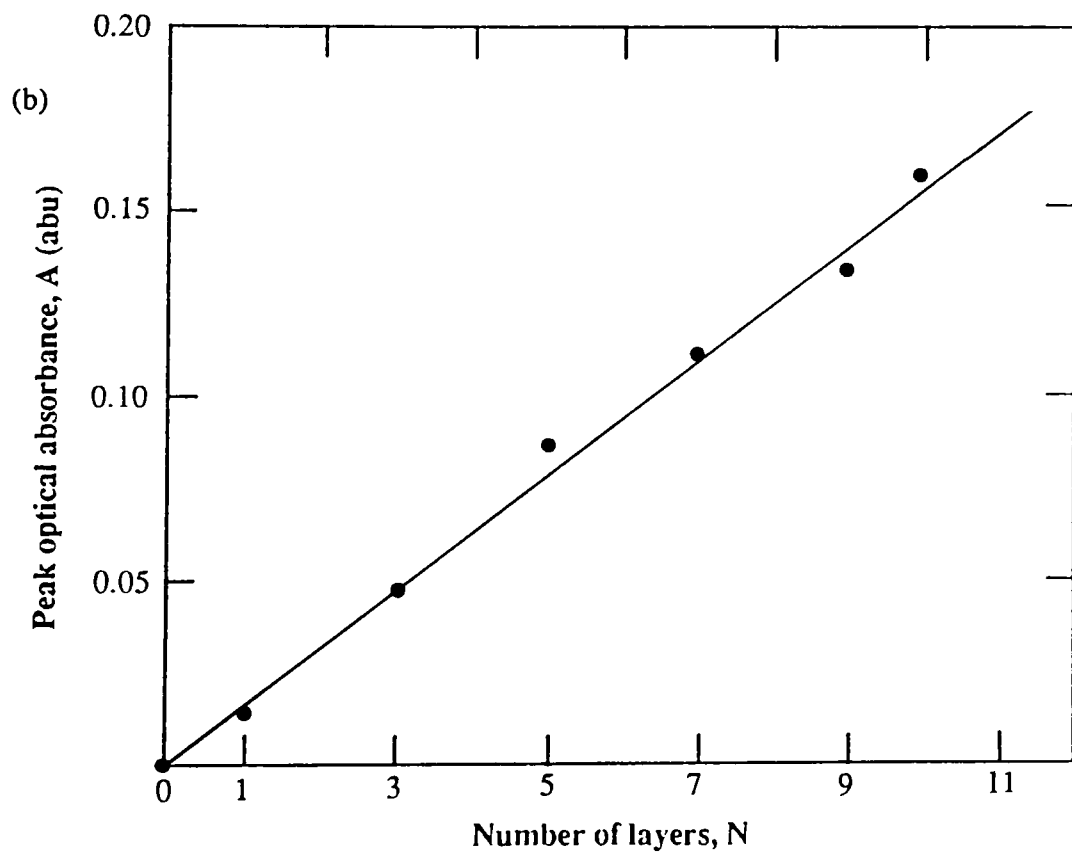
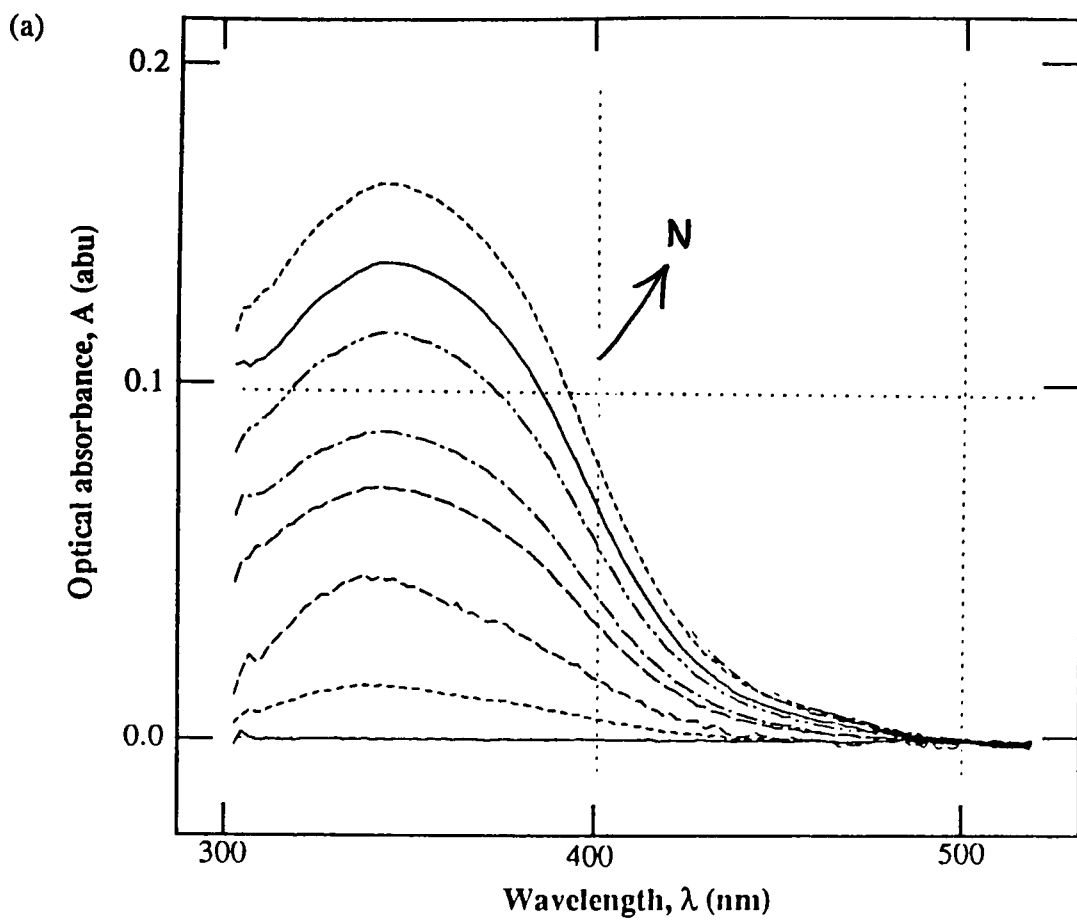


Figure 6.3 : Uv-visible spectroscopic characterisation of $\text{Ru-}\phi\text{-C}_2\phi\text{-OC}_{14}$ LB films. (a) absorption spectra for $N=0-11$ layers and (b) the peak absorbance versus N .

(thickness), N , showing the linear relationship and confirming that monolayers of the same optical properties have been transferred reproducibly. The maximum absorption occurs at 344nm and the absorbance per monolayer is 0.0152. It is interesting to note that the $\lambda_{\text{max}}^{\text{LB}}$ is approximately 11nm lower than the wavelength corresponding to the lowest energy transition in the solution (chloroform) but identical to that observed in the compressed Langmuir film (356nm). It may be concluded that this small hypsochromic shift with respect to the solution value occurs because of the relatively close, energetically unfavourable approach of molecular dipoles in the compact Langmuir and LB layers. The result is a lowering of the ground state dipole moment (in order to minimise dipole-dipole repulsions) relative to the excited state which leads to a larger transition energy. Much larger hypsochromic shifts (>100nm) are observed with hemicyanine derivatives researched by Neal *et al* [108]. However, the small shift observed in the case of Ru- ϕ -C₂"'- ϕ -OC₁₄ is not surprisingly low as the active dipole moments (along the acetylene ring system) are prevented from approaching each other extremely closely by steric hinderance from adjacent ruthenium (η^5 -cyclopentadienyl)-(bis triphenylphosphine) groups such that the dipole - dipole repulsion remain relatively weak. In the hemicyanine situation, the area per molecule on the water surface is approximately 0.3nm², and the dipoles of adjacent molecules are extremely close together in the LB film such that the dipolar repulsion is large as is the resultant perturbation to the transition energy.

In Table 6.2, the peak absorption wavelength of the transferred LB film is given and compared to values for the solution and the floating Langmuir film for several organo-ruthenium complexes. In all cases in Table 6.2, the LB spectra were recorded for 3 layer samples using the Z-type deposition scheme in which the substrate is lowered through the air-water interface at low (often zero) surface pressure. It is evident that for several of the complexes, such as Ru- ϕ -N₂"'- ϕ -NMeC₇ and Ru- ϕ -N₂"'- ϕ -OC₁₆, the changes in transition wavelength are relatively large, while for Ru- ϕ -OC₁₂ and Ru- ϕ -NMeC₁₄ the changes are small. The complexes Ru- ϕ -N₂"'- ϕ -NMeC₇ and Ru- ϕ -N₂"'- ϕ -OC₁₆ also

Complex	solution λ_{max} nm	Langmuir λ_{max} nm	LB λ_{max} nm	a_1 abu	LB-soln $\Delta\lambda_{\text{max}}$ nm
Ru-ϕ_2-OC₁₂	332	327	340	0.0150	+8
Ru-ϕ-NMeC₁₄	337	330	337	–	0
Ru-ϕ-C''₂-ϕ-OC₁₃	368	356	358	0.0097	-10
Ru-ϕ-C'''₂-ϕ-OC₁₄	355	356	344	0.0152	-11
Ru-ϕ-N''₂-ϕ-NMeC₇	498	480	480	0.0120	-18
Ru-ϕ-N''₂-ϕ-OC₁₆	383	352	351	0.0100	-32

Table 6.2 : A comparison of the wavelengths of maximum absorption for several organo-ruthenium complexes in solution, Langmuir film and LB film form.

deposit in the Z*-type configuration (that is even through a compressed layer on the downstroke) and show the largest shift between the LB film λ_{max} and the solution λ_{max} ($\Delta\lambda^{\text{LB-sol}}$). If dipolar relaxation were to occur within the transferred LB film during or after deposition, the difference in the $\lambda_{\text{max}}^{\text{LB}}$ and $\lambda_{\text{max}}^{\text{L}}$ (Langmuir film) values would be expected to be large. However, virtually no difference is observed for these complexes indicating that the dipolar alignment properties of the floating layer are maintained in the transferred solid structure. However, compounds Ru- ϕ -C₂₂- ϕ -OC₁₃, Ru- ϕ -OC₁₂ and Ru- ϕ -NMeC₁₄ show a red-shift of the $\lambda_{\text{max}}^{\text{LB}}$ value relative to the floating layer transition indicating that some dipolar rearrangement has possibly occurred. It is important to note that in these cases, the compressed Langmuir films may be transferred in the pseudo-Y-type configuration (Y*) in addition to the usual Z-type mode. This implies that the molecular dipoles may prefer to assemble symmetrically which is consistent with the possibility of rearrangement of Z-type structures after deposition.

(ii) Alternate layer film characterisation.

It was mentioned in section 6.2.2 that all the organo-ruthenium complexes in this class specifically designed for LB deposition can be alternated with behenic acid to yield polar ABABA structures. It is also convenient to use the uv-visible absorption technique to assess the reproducibility of deposition when producing such structures. The behenic acid molecules do not absorb radiation in the range 300–800nm and, therefore, the absorption of the acid monolayers may be neglected. Figure 6.4 shows the spectra for various thicknesses of alternate layer LB films of the complex Ru- ϕ -NMeC₁₄ and the linear relationship between the peak absorbance wavelength and the number of active deposited ruthenium layers.

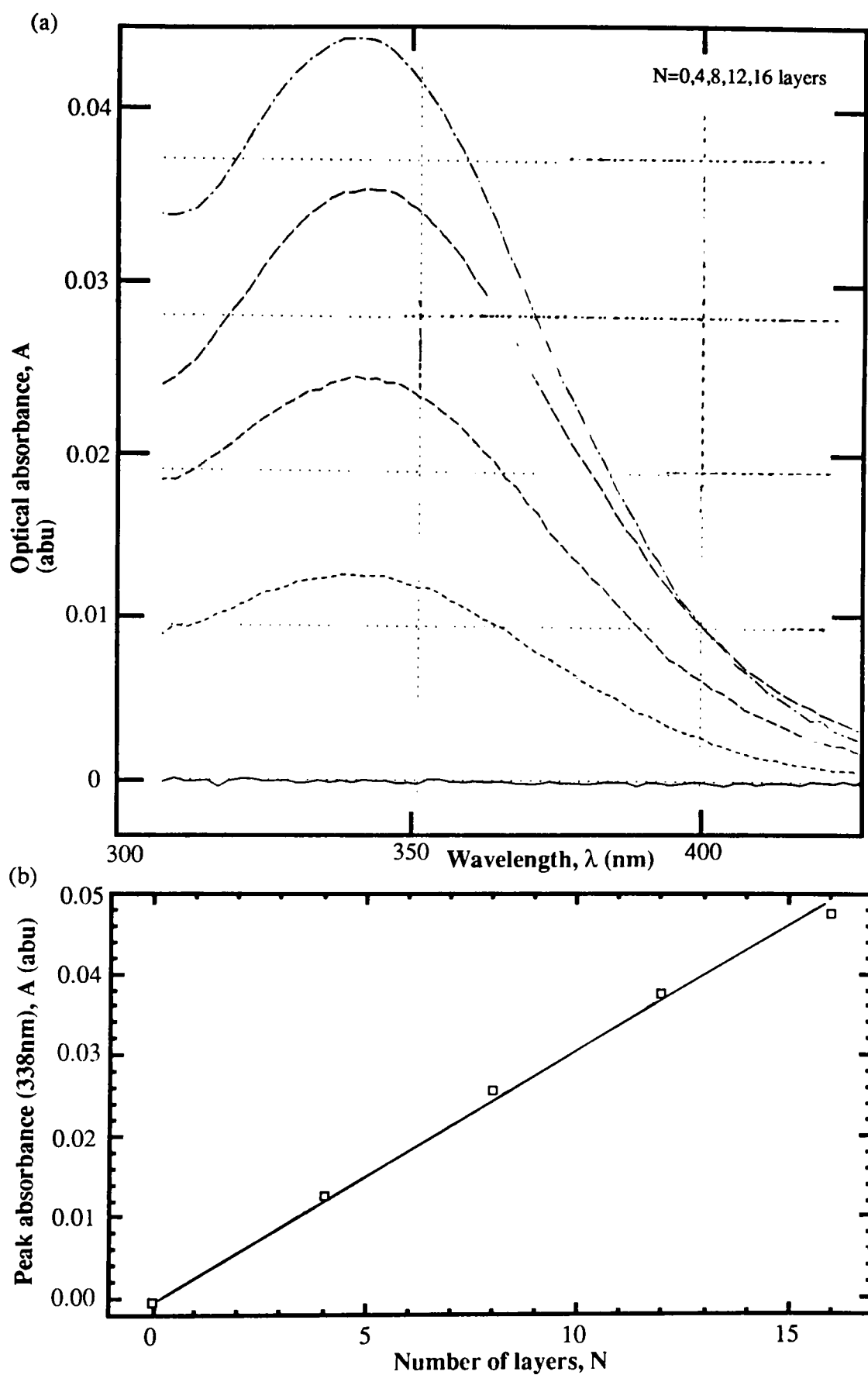
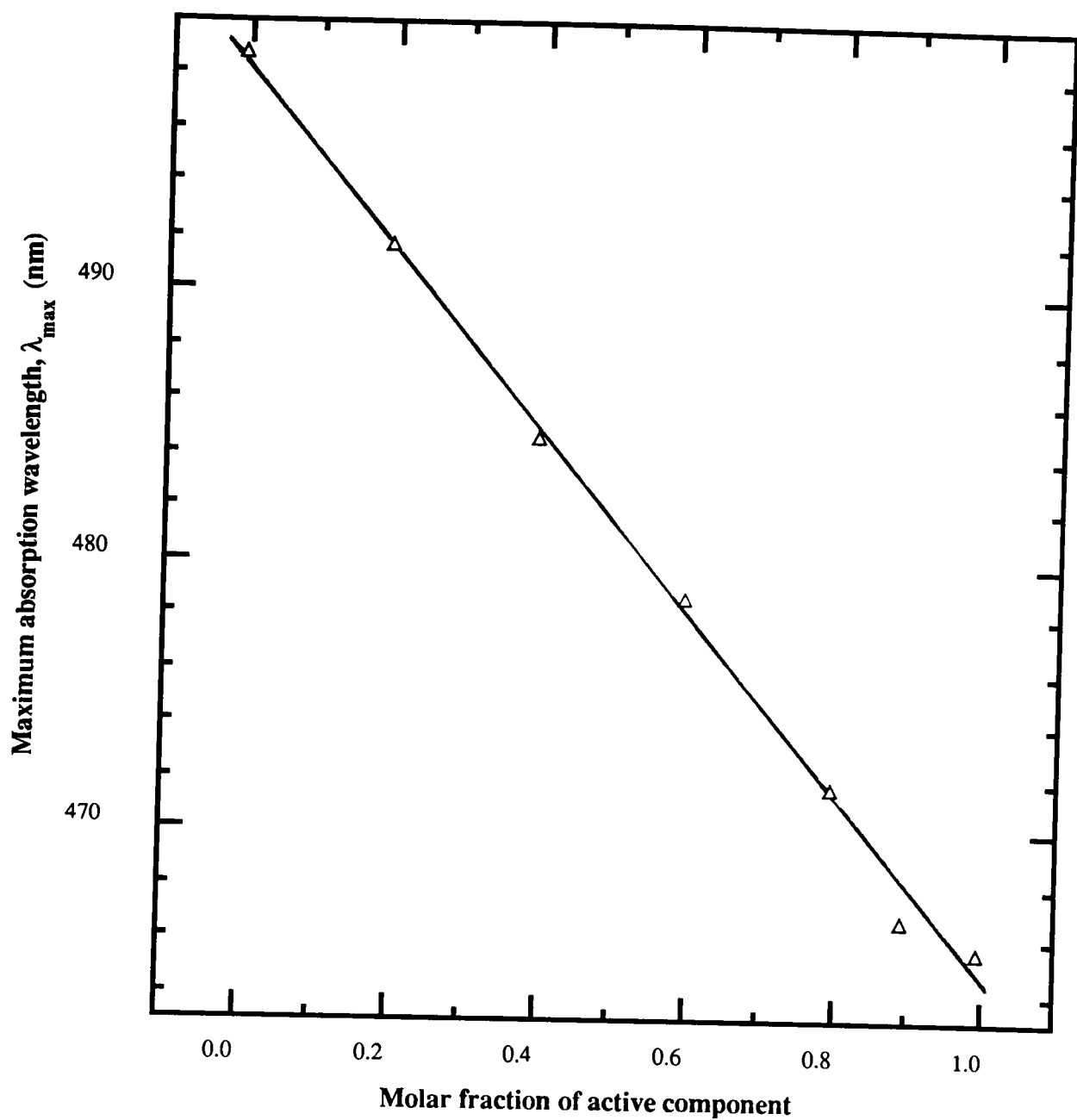


Figure 6.4 : (a) Absorption spectra of alternate layers of $\text{Ru-}\phi_2\text{OC}_{12}$ and behenic acid and (b) the peak absorbance (338nm) versus the number of transferred layers.

(iii) Absorption characterisation of heterogeneous organo-ruthenium LB films.

The shifts produced in the transition energies of the solutions, Langmuir films and LB monolayers and multilayers occur as a result of a changing environment in which the molecules reside. For instance, it has been shown in this thesis that the alignment of dipoles within a Langmuir or LB film often causes the dipole-dipole interactions to increase significantly compared to the solution in which the dipolar interactions are relatively small.

It is possible to observe the perturbation to the transition energies within transferred heterogeneous monolayer films in which the ruthenium complex co-exists with behenic acid molecules. As the relative fraction of behenic acid rises, the average separation of adjacent ruthenium molecules increases thus reducing the dipole-dipole interactions and producing a bathochromic shift in the peak absorption wavelength. This can be seen in Figure 6.5 for complex $\text{Ru-}\phi\text{-N}_2^{\text{''}}\text{-}\phi\text{-NMeC}_7$. The dipole-dipole interactions are large as the $\text{Ru-}\phi\text{-N}_2^{\text{''}}\text{-}\phi\text{-NMeC}_7$ molecules may approach each other closely for high molar fractions in the mixed layer. The main advantage of mixing active dye molecules with an acid to form a mixed monolayer is that, usually, the molecular order within the structure improves as does the efficiency with which deposition can occur. Therefore, it is possible to find a mixture whose deposition quality is optimum and the number of active ruthenium molecules per unit area is maximised. However, too much attention has not been given to the optimisation of the deposition conditions for heterogeneous layers in this thesis as their major disadvantage lies in their inherently reduced thermal stability.



△ Complex $\text{Ru-}\phi\text{-N}_2^{\text{''}}\text{-}\phi\text{-NMeC}_7$

Figure 6.5 : Mixed layer investigation showing the shift in $\lambda_{\max}$ deposited monolayers of the $\text{Ru-}\phi\text{-N}_2^{\text{''}}\text{-}\phi\text{-NMeC}_7^{\text{x}}$: behenic acid^y system.

(iv) Optical interference phenomena.

The technique of uv-visible spectroscopy has proved to be an extremely useful tool in the characterisation of novel materials in solution, Langmuir film or LB film form. However, it must be remembered that optical interference effects become important when thicknesses approaching the quarter wavelength are to be investigated. The reflectance of a surface (such as a glass slide or a silicon wafer) may be dramatically modified by the application of thin film optical coatings [109] provided their thickness is tuned to correspond precisely to that required to produce totally constructive or totally destructive interference at the reflecting boundaries of the structure. Figure 6.6a shows the principle of obtaining high reflectance and anti-reflecting coatings using thin film technology. Langmuir and Blodgett themselves produced such coatings on spectacles and glass instrument panel covers to minimise glare [110] and showed how the LB technique enabled precise thicknesses to be realised accurately. However, when using a spectrophotometer to measure absorption the change in the reflectance properties are actually *observed* by the detector as modifications to the *absorption* of the sample. For instance, a substrate coated with a high-reflectance layer reflects an additional few percent of the incident light from the sample surface. This results in a relative change in the intensity of the light beam that passes through the sample. The detector is therefore deceived into measuring a decreased absorption, although this gain in intensity is actually a result of increased surface reflectance. As an example, Figure 6.7 shows a plot of "apparent" absorption versus the number of layers of a 1:1 Ru- ϕ -OC₁₇ : behenic acid heterogeneous LB film. Clearly, the curve is a modification of the expected linear Beer-Lambert relationship by the sinusoidal reflectance fringes. The maxima and minima are exposed and occur at about 20 and 40 layers respectively. Clearly, consideration must be given to these effects when interpreting absorption data. Alternative characterisation techniques are used when studying relatively thick (> 20 layers) LB films to avoid these complications.

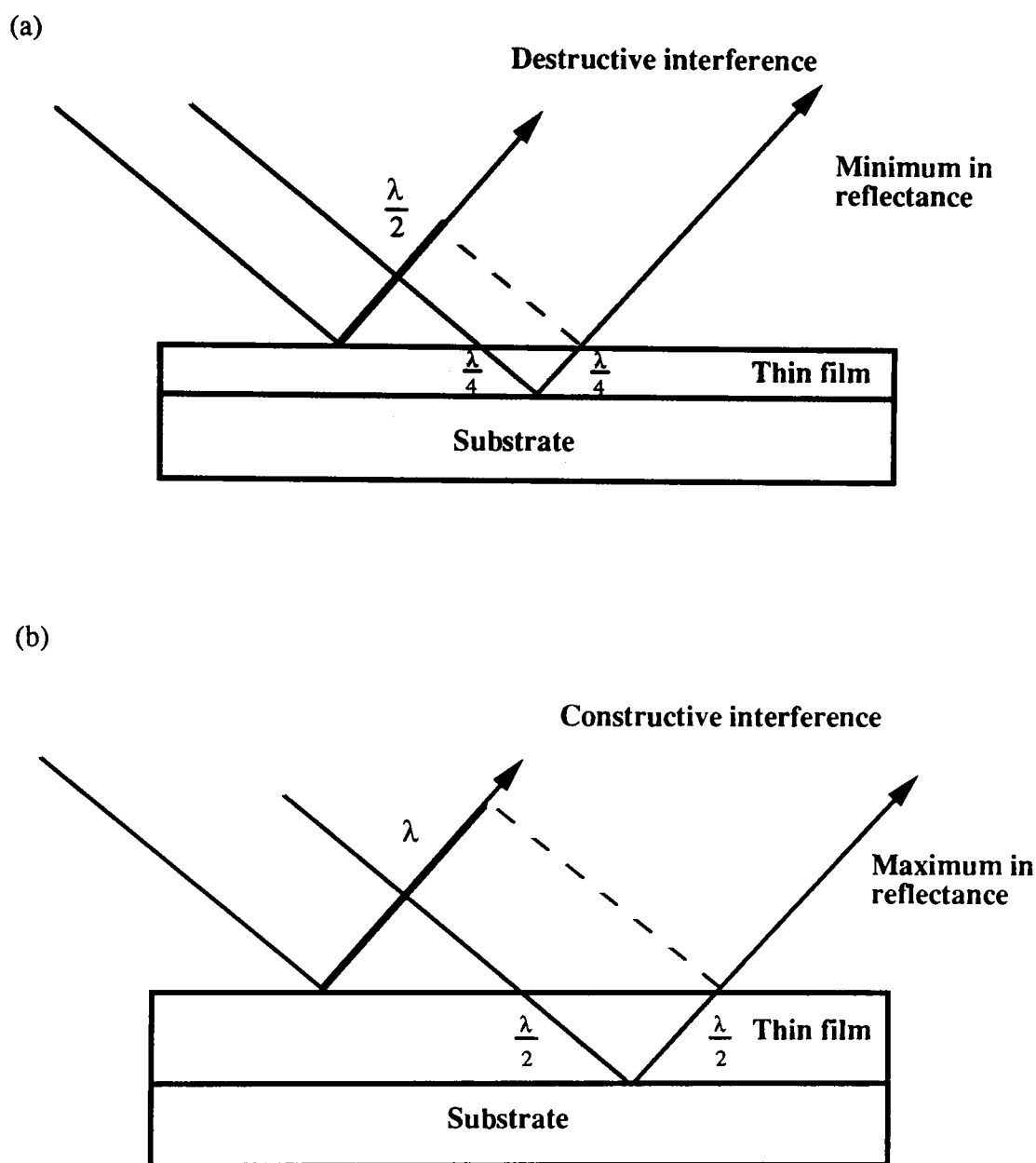


Figure 6.6 : The anti-reflectance and high reflectance properties of thin optical coatings.
 (a) Anti-reflectance for quarter wavelength films and (b) the high reflectance of films of integer wavelength in thickness.

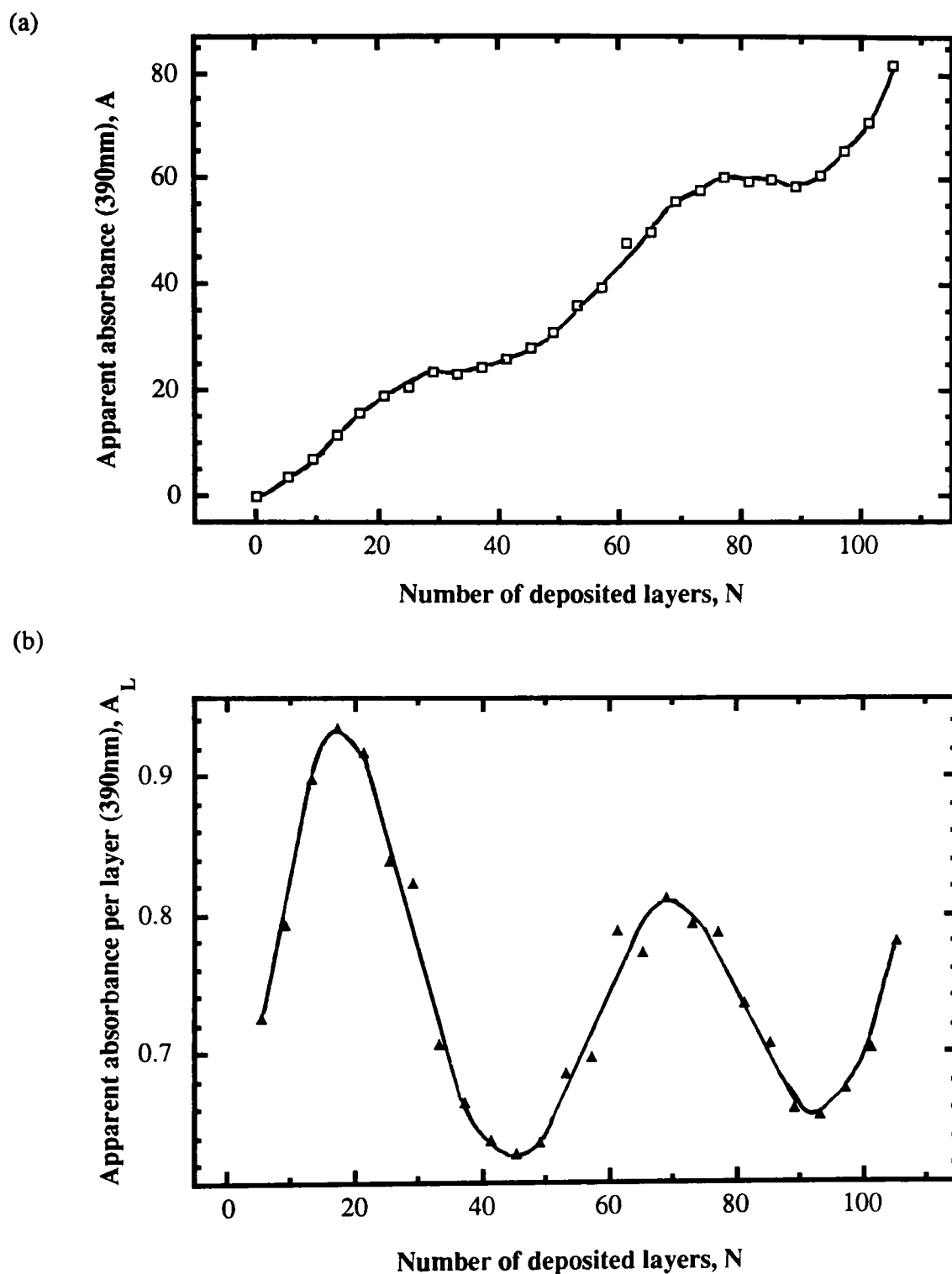


Figure 6.7 : Optical interference effects exhibited by "thick" LB films. (a) The absorbance at 390nm versus number of layers of a $\text{Ru-}\phi\text{-OC}_{17}^{40}$: fatty acid⁶⁰ LB film and (b) the apparent absorbance per monolayer as a function of the number of layers showing the minima and maxima due to reflectance variation.

In conclusion to section 6.3.1, the spectral characteristics of LB films of novel organo-ruthenium complexes have been investigated in order to determine the quality and reproducibility of the successive transfer of floating monolayers onto a solid substrate. The transition energies of the solid LB layers have been compared to the values for the Langmuir films and the spreading solutions. For some materials, especially those which transfer in the Z-type configuration only (neglecting alternate layer deposition), a blue-shift is observed for the LB film with respect to the solution indicating that the alignment of molecular dipoles has induced perturbations in the molecular energy levels due to dipole-dipole repulsion. The importance of considering optical interference effects has also been stressed.

6.3.2 Thickness and refractive index determination.

For any optical application, it is important to be able to determine accurately the refractive index and the optical thickness of a material which will form an essential component of an optical device. Two optical techniques have been used to perform this task: ellipsometry and the surface plasmon resonance technique. Both methods will be discussed in this section.

(i) Ellipsometric characterisation.

The principle of the technique of ellipsometry has been previously described in Chapter 4. It has been used here to measure the thickness of Z-type multilayer LB films of several organo-ruthenium complexes. Figure 6.8 shows plots of the total film thickness of complexes $\text{Ru-}\phi_3\text{-C}_5$, $\text{Ru-}\phi\text{-C}_{12}$ and $\text{Ru-}\phi_2\text{-OC}_{12}$ as a function of the number of transferred layers, N , measured at 633nm. Clearly, the relationships show that the film thickness varies linearly with N as expected and thus provide further evidence that the deposition technique is highly reproducible. The resulting thickness per layer yields useful

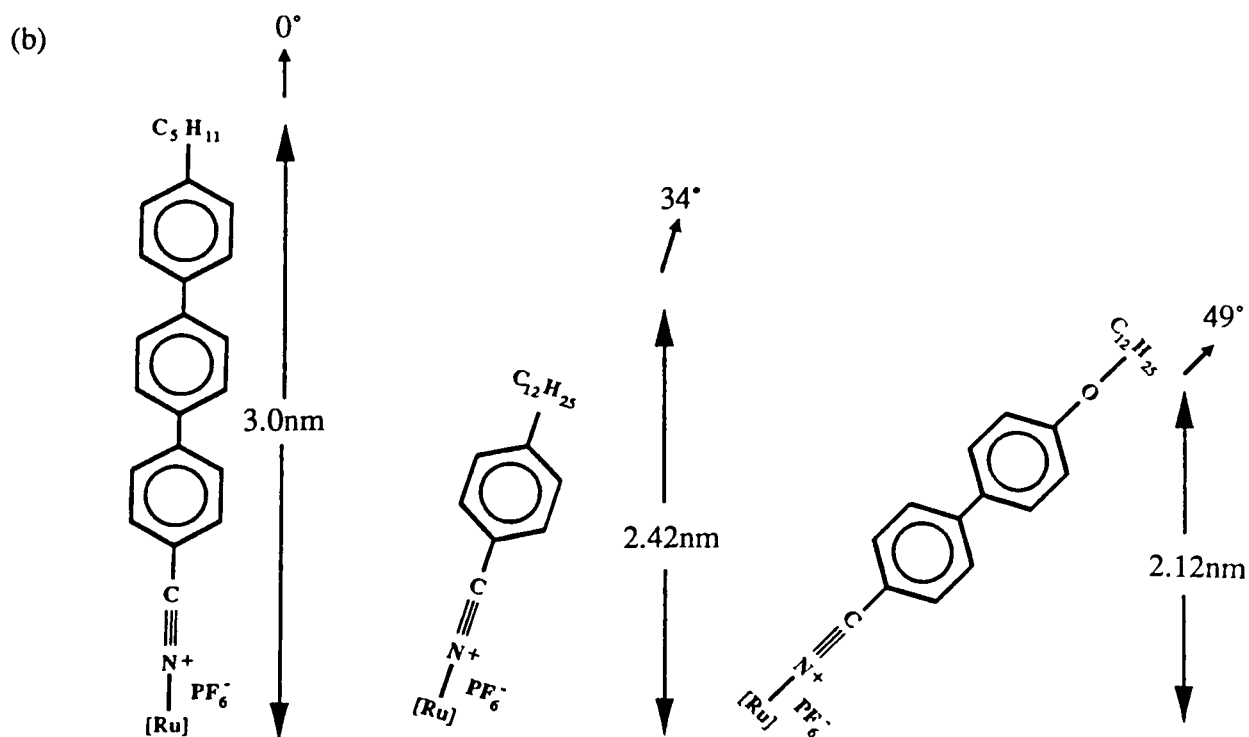
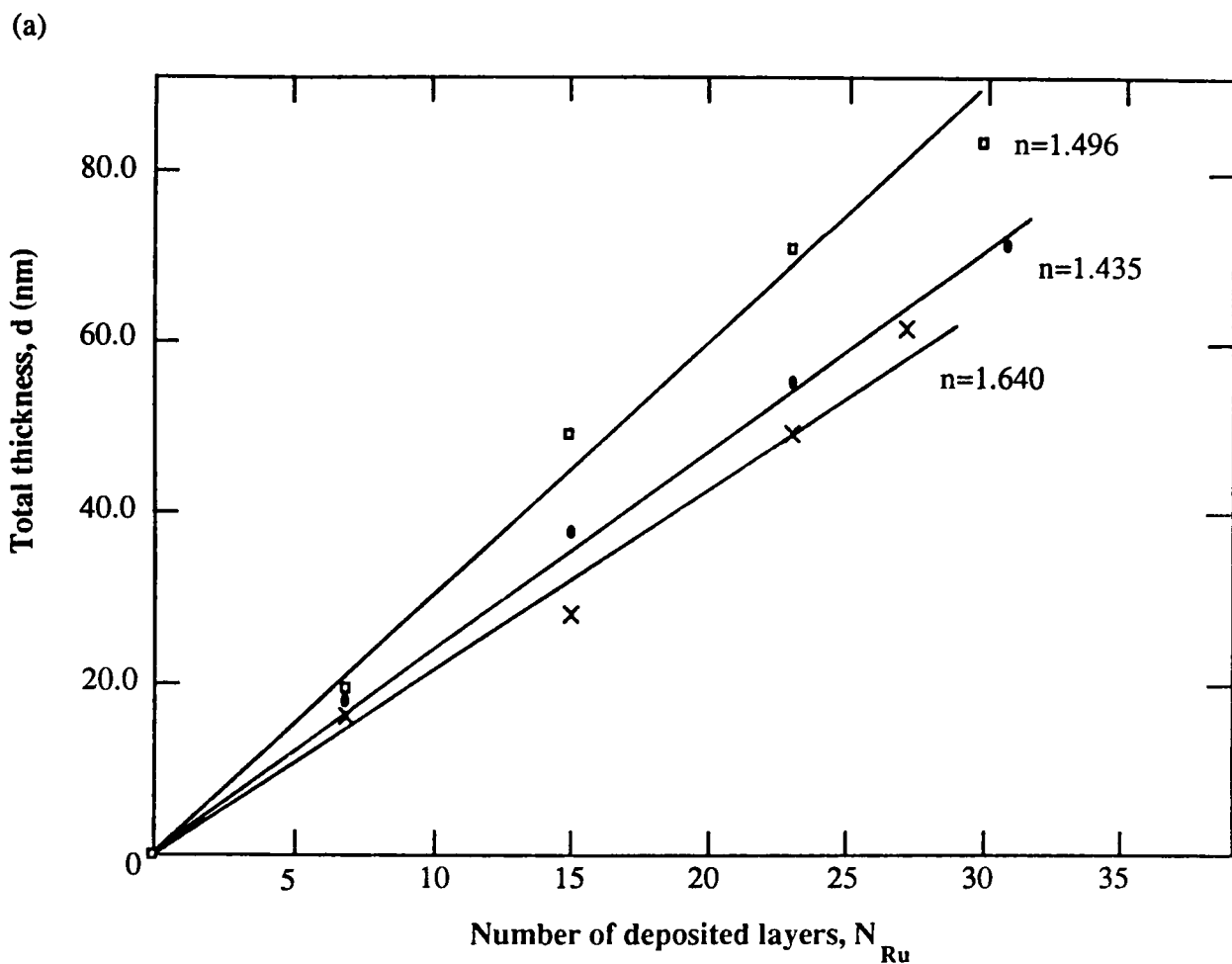


Figure 6.8 : Ellipsometric characterisation of organo-ruthenium LB films. (a) film thickness versus number of transferred layers and (b) possible tilting structure.

information concerning the possible orientation of the molecules with respect to the normal to the substrate plane. The molecular length of the complexes estimated using space-filled molecular modelling techniques are 3.0nm, 2.9nm and 3.4nm respectively. However, the measured thickness per monolayer values are 3.0nm, 2.4nm and 2.1nm respectively indicating that for Ru- ϕ -C₁₂ and Ru- ϕ 2-OC₁₂, the molecules must be tilted relative to the normal to the plane of the substrate, whereas the identical values for Ru- ϕ ₃-C₅ imply a vertical orientation. Many researchers have previously proposed that certain LB films are composed of arrays of tilted molecules [111]. It is interesting to observe that the three complexes described above exhibit an increased tilt angle as the ground state dipole moment progressively increases. This leads to the hypothesis that the molecules may tilt in an attempt to reduce the intermolecular dipole-dipole repulsion. Further structural analysis involving X-ray diffraction and RHEED is currently in progress to establish the detailed molecular arrangement within the LB film.

(ii) Surface plasmon reflectometry.

The surface plasmon resonance approach to thickness determination has enabled an accurate measurement of the thickness and refractive index (at 633nm) to be performed on an LB monolayer of complex Ru- ϕ ₃-C₅. Figure 6.9 shows the reflectivity of the incident HeNe laser beam as a function of incidence angle for (a) a bare silver film and (b) a silver film coated with a monolayer of Ru- ϕ ₃-C₅. Clearly, at a specific angle, θ_R , the reflectivity falls dramatically to a very low value indicating that energy has been coupled into the surface plasmon modes of the silver surface from the incident laser beam. Also, a shift in resonance angle is observed when the silver surface is modified with a deposited monolayer. Much theoretical curve fitting has been performed by Mr. S. Cooke in the Oxford Molecular Electronics Group to enable the experimental curves to yield useful information regarding the thickness and refractive index of the layer. For the Ru- ϕ ₃-C₅ complex, a thickness of 3.0 nm and a real part of refractive index of 1.51 were obtained.

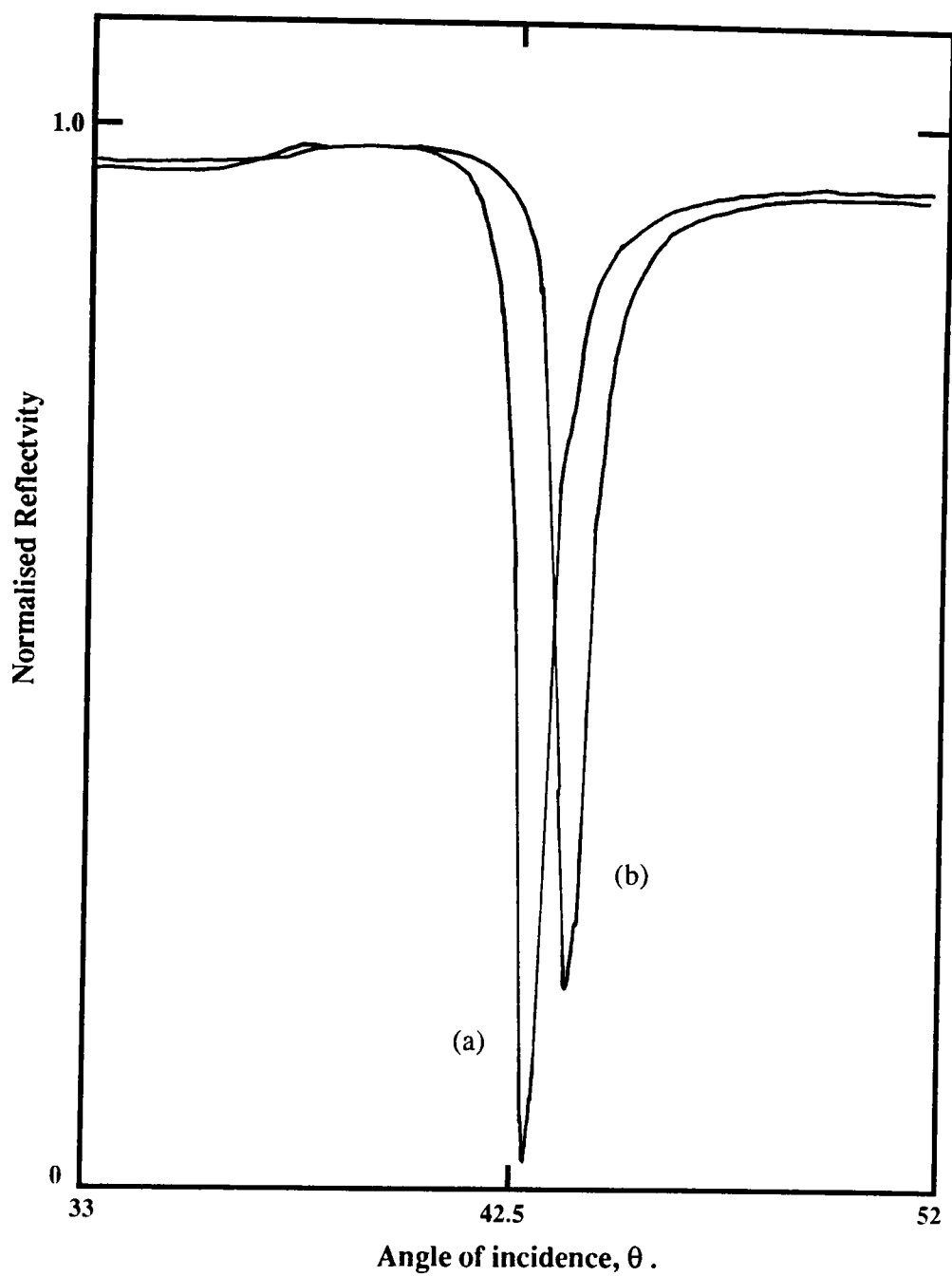


Figure 6.9 : Surface plasmon reflectometry of (a) a bare silver film and (b) an Ag substrate coated with a monolayer of complex $\text{Ru-}\phi_3\text{C}_5$.

This thickness per layer is in excellent agreement with the value obtained using ellipsometry. Further work is continuing to measure the layer thicknesses and refractive indices of several other complexes in order to obtain additional information regarding the organisation of the organo-ruthenium molecules within monolayer and multilayer films.

6.4 Electrical properties of organo-ruthenium LB films.

In this section, the piezoelectric quartz crystal resonance technique has been shown to be invaluable in characterising the deposition of several organo-ruthenium complex LB films. Also the capacitance of metal - LB film - metal structures has been measured and information regarding the dielectric thickness inferred. An attempt to measure the lateral electrical conductivity has been made although unsuccessfully.

6.4.1 Piezoelectric quartz crystal resonance frequency modification by LB films.

The principles of the use of the oscillation properties of single crystal, piezoelectric quartz transducers in characterising LB deposition have been described in detail in Chapter 4. It was seen that the resonant oscillation frequency could be changed dramatically by the deposition of LB films onto the transducer electrodes. The resultant shift in frequency, Δf , may be written as:

$$\Delta f = \frac{2f_0^2 N \delta\mu}{\rho_q v_q} \quad (6.1)$$

where N = the number of layers, f_0 = the initial resonance frequency, $\delta\mu$ = the mass per unit area per layer, ρ_q = density of quartz and v_q = the speed of an acoustic wave through the quartz. Therefore, a linear relationship between Δf and the number of transferred layers is expected provided uniform and reproducible deposition has occurred. Figure

6.10 shows plots of Δf versus N for several organo-ruthenium LB films. Clearly, the linear relationships confirm that equal mass per unit area has been deposited onto the devices during each transfer of a monolayer. The gradients show that for 6MHz oscillators, typical frequency shifts of about 50Hz per layer are detected. It is not sensible to compare the frequency changes per layer of each complex when different piezoelectric substrates have been used because of variations in the surface area of the silver electrodes. However, Figure 6.11a depicts the frequency change produced by LB films of several complexes when the multilayers of different materials are *successively* stacked onto the *same* quartz oscillator. In this way, the possible surface area variations from one device to another are eliminated and relative surface densities can be measured.

It is clear that a linear relationship is maintained for each complex and, from Figure 6.11b, the frequency shift is proportional to the ratio of the relative molar mass and the area per molecule. This result demonstrates the extreme sensitivity of the measurement technique. The typical mass of a ruthenium monolayer is approximately 200 ngcm⁻² which normally causes a frequency change of about 50Hz (for $f_0=6\text{MHz}$). A minimum frequency shift of say 2-3Hz is detectable so that the technique is capable of measuring masses as low as 12ng using 6MHz crystals although added sensitivity may be obtained using higher frequency resonators.

It is of interest to observe the behaviour of the frequency shift for mixed monolayer systems such as Ru- ϕ -OC₅ : behenic acid and the novel mixture Ru- ϕ_3 -C₅ : NC- ϕ_3 -C₅ in which the precursor molecules are situated in the voids between the terphenyl chains of adjacent ruthenium molecules. Firstly, Figure 6.12a shows the plots of Δf versus N for Ru- ϕ -OC₅ when Z-type deposition is attempted and for the heterogeneous Ru- ϕ -OC₅⁷⁵ : behenic acid²⁵ system. Clearly, an improvement in linearity is observed for the mixed system indicating that the reproducibility of deposition is enhanced with the use of only a relatively low molar fraction of fatty acid. The technique is useful, therefore, to

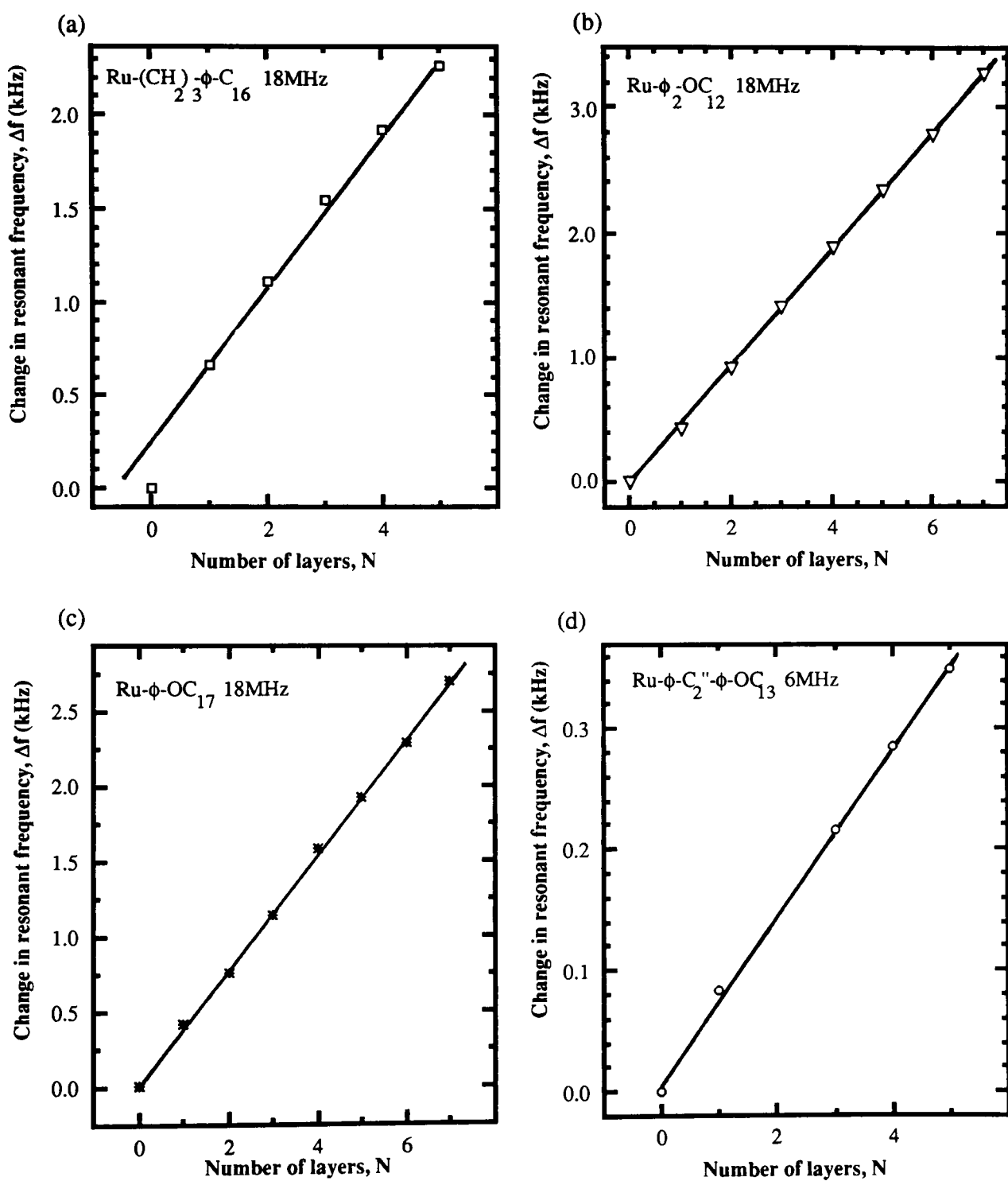


Figure 6.10 : Quartz crystal oscillator characterisation of organo-ruthenium LB films.

(a) $\text{Ru}-(\text{CH}_2)_3-\phi-\text{C}_{16}$, (b) $\text{Ru}-\phi_2-\text{OC}_{12}$, (c) $\text{Ru}-\phi-\text{OC}_{17}$ and (d) $\text{Ru}-\phi-\text{C}_2''-\phi-\text{OC}_{13}$

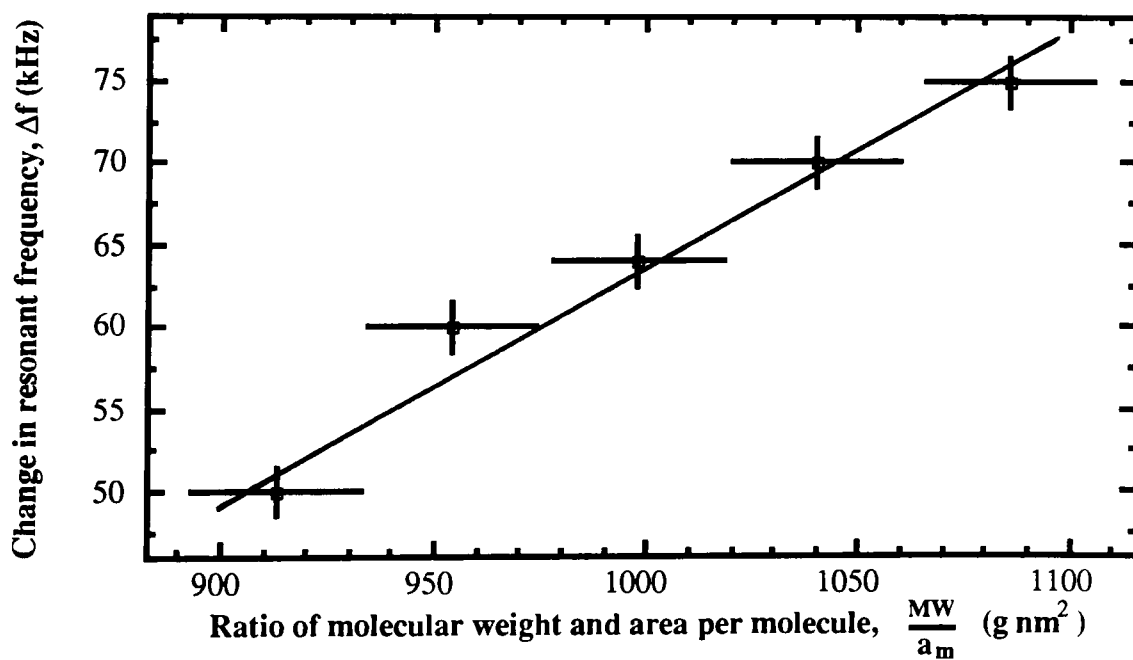
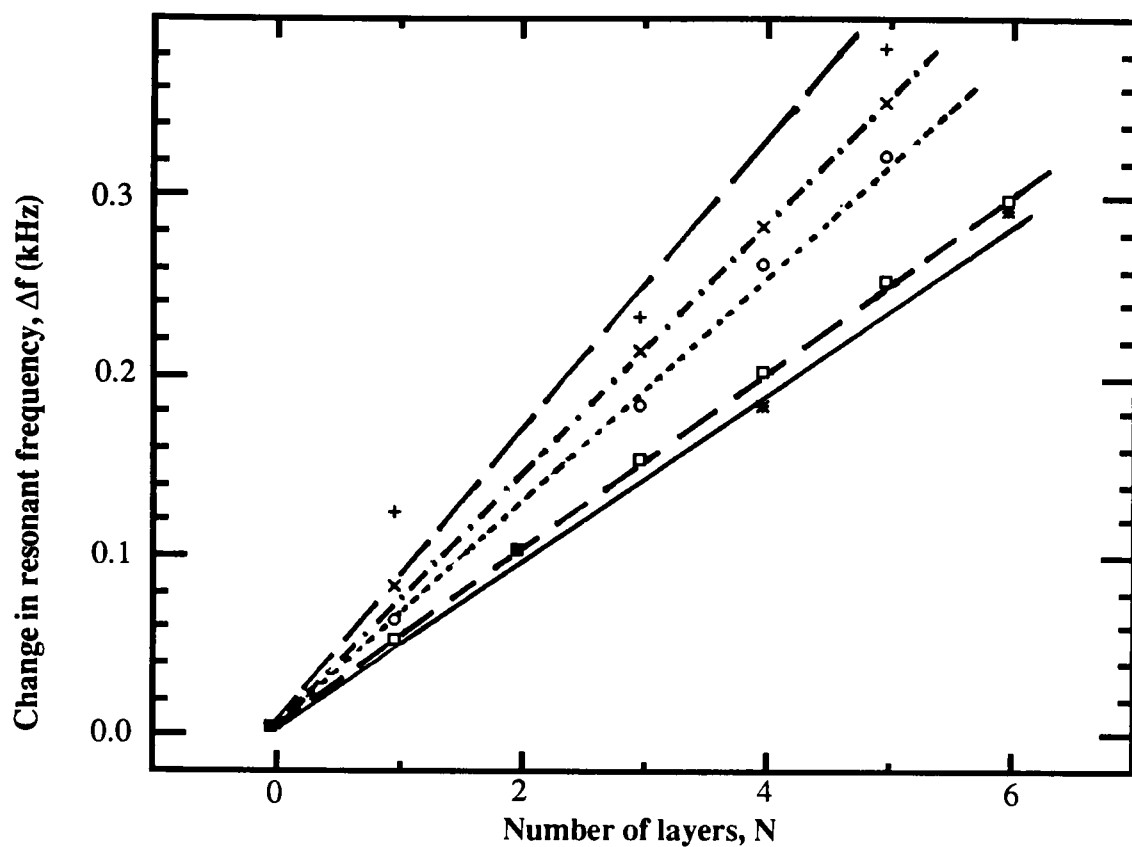


Figure 6.11 : Resonant frequency change of piezoelectric quartz oscillator by mass-loading of multilayer organo-ruthenium LB films successively on the same device. (a) Δf versus N plots and (b) the frequency change as a function of molecular weight per unit area.

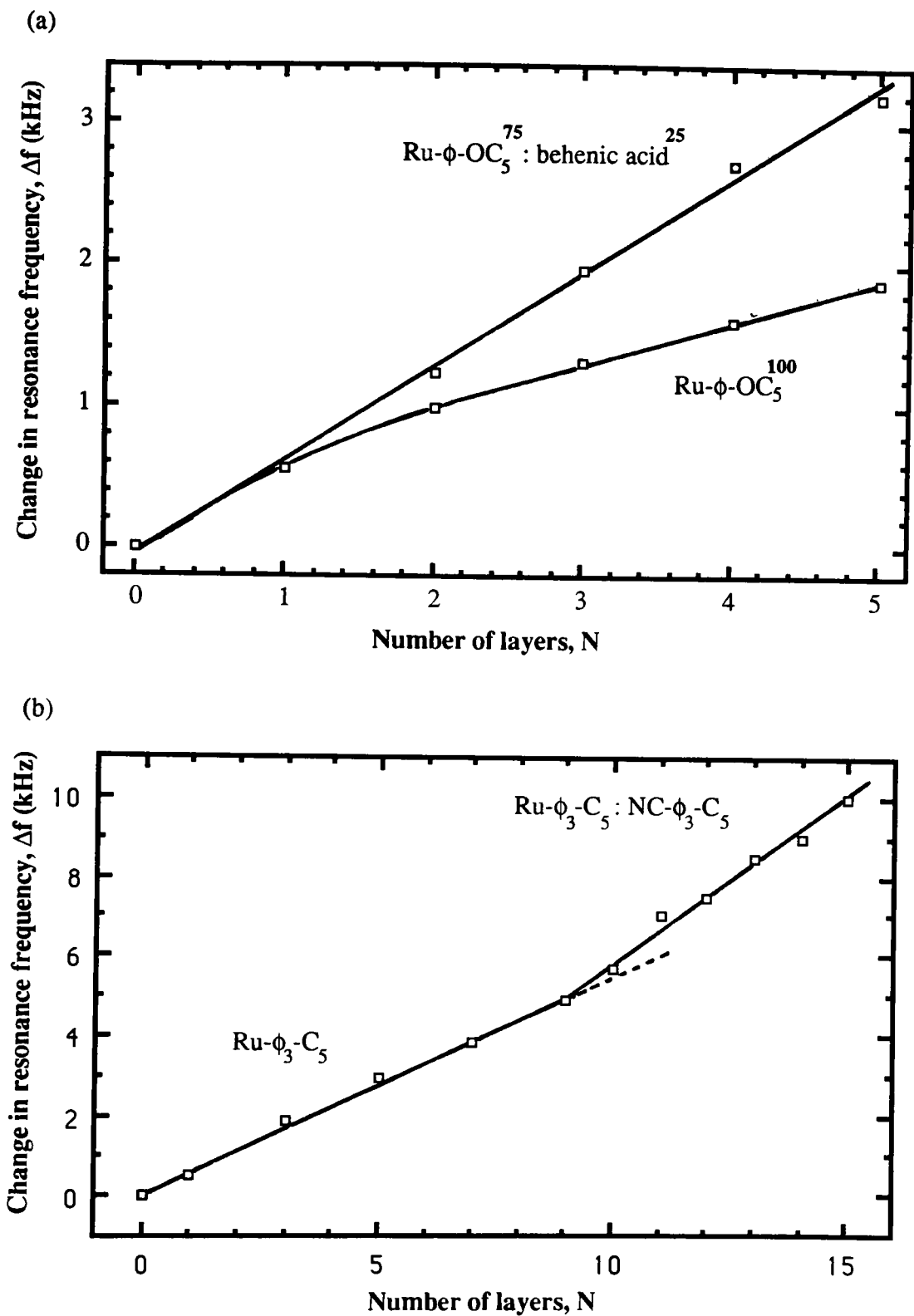


Figure 6.12 : Piezoelectric quartz crystal characterisation of heterogeneous LB films.
 (a) The improvement of deposition obtained by mixing Ru- ϕ -OC₅ with a small amount of behenic acid and (b) the increase in mass per unit area per layer measured from high density incorporation structures.

find the minimum possible molar ratio of behenic acid to realise a linear Δf versus N profile and thus to maximise the density of ruthenium molecules in the layer.

This method has also provided further evidence that precursor molecules can be incorporated into the ruthenium lattice. Figure 6.12b shows Δf initially for 1-9 deposited monolayers of complex $\text{Ru-}\phi_3\text{-C}_5$ followed by the subsequent transfer (on top of the first multilayer on the same oscillator) of 6 monolayers of the mixture $\text{Ru-}\phi_3\text{-C}_5^{35} : \text{NC-}\phi_3\text{-C}_5^{65}$. The change in gradient that occurs after deposition of the first mixed layer is indicative that it possesses a higher mass per unit area which is expected if incorporation has occurred. For the case in which no space-filling results, the gradient would not be expected to show a significant change. Each organo-ruthenium molecule would simply be replaced by several precursors of lower mass such that the mass per layer would remain largely unaffected.

In conclusion, the technique has therefore provided invaluable information concerning the quality of deposition of the ruthenium complexes, and has proved to be sufficiently sensitive to detect changes in the surface density of different complexes as low as approximately 4 ngcm^{-2} . Finally, the incorporation of nitrile precursors into the $\text{Ru-}\phi_3\text{-C}_5$ lattice has been exposed by this characterisation method.

6.4.2 Capacitance measurements of organo-ruthenium LB films.

In Chapter 4, the use of capacitance measurements to characterise the deposition of LB films was described. Indeed, the technique provides information concerning the dielectric thickness (d/ϵ_r) of the material and also the uniformity of the film across the surface area of the substrate. Normally, the LB layer is deposited onto an aluminium base electrode so that consideration must be given to the inherent oxide capacitance. Extreme care must be taken to evaporate the top electrodes onto the LB film surface. If the

evaporation rate is too high, the heating effect on the organic film causes structural damage and, in severe cases, electrical shorting. The deposition of the electrodes usually takes several hours as the rate is suppressed to $0.01 - 0.05 \text{ nms}^{-1}$ and the metal is evaporated in only 1.0nm stages every 20 minutes in order to ensure no damage occurs.

Figure 6.13 shows a plot of inverse capacitance versus the number of deposited layers for 4 ruthenium complexes $\text{Ru-}\phi\text{-C}_{12}$, $\text{Ru-}\phi\text{-OC}_5$, $\text{Ru-}\phi\text{-OC}_{12}$ and $\text{Ru-}\phi\text{-OC}_{17}$. Table 6.3 gives the dielectric thickness for each complex and the estimated dielectric constant based on an approximation to the layer thickness. The $\text{Ru-}\phi\text{-C}_{12}$ monolayer is estimated to be 2.42nm as measured using ellipsometry and those of $\text{Ru-}\phi\text{-OC}_n$ (with $n=5,12,17$) to be 1.38nm, 1.84nm and 2.18nm respectively if a tilt of 30° is assumed. Clearly, reproducible deposition has occurred. The intercepts all lie in the range $0.92 < 1/C < 1.24 \text{ nF}^{-1}$ which is consistent with the value expected from the aluminium oxide layer. The dielectric thickness is much lower for the alkoxy ($\text{Ru-}\phi\text{-OC}_n$) series than the $\text{Ru-}\phi\text{-C}_{12}$ complex and thus the calculated dielectric constants are correspondingly larger. This result can be explained by considering the relative magnitudes of the ground state dipole moments of both types of complex. The alkoxy dipole moment is larger than the $\text{Ru-}\phi\text{-C}_{12}$ complex and thus, at a constant frequency, changes in the orientation of the molecules (as they follow the a.c. field) produce a larger polarisation change relative to that produced by the $\text{Ru-}\phi\text{-C}_{12}$ compound.

In the near future, it will be possible to routinely measure the capacitance of LB film structures as a function of frequency in the 5Hz - 13MHz range at the Oxford Molecular Electronics laboratory. It is envisaged that a systematic study of the dielectric response of all the ruthenium compounds will be undertaken and yield exciting data concerning the dielectric relaxations that occur. This information will be of invaluable use in furthering the understanding of the mechanistic origin of pyroelectricity in these materials.

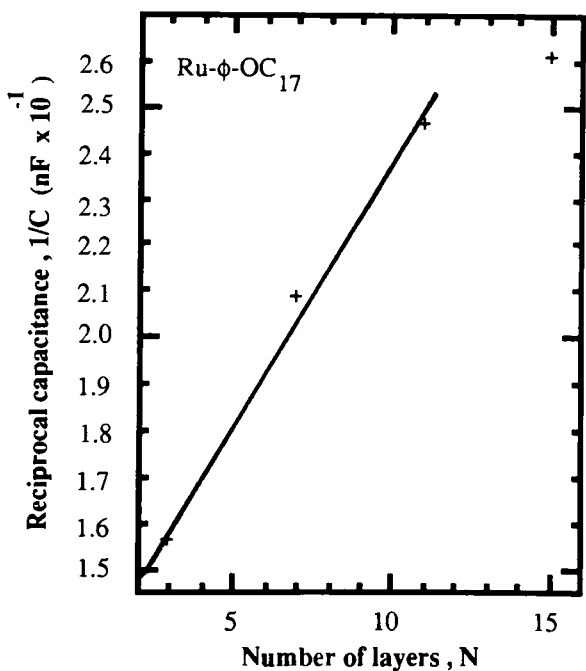
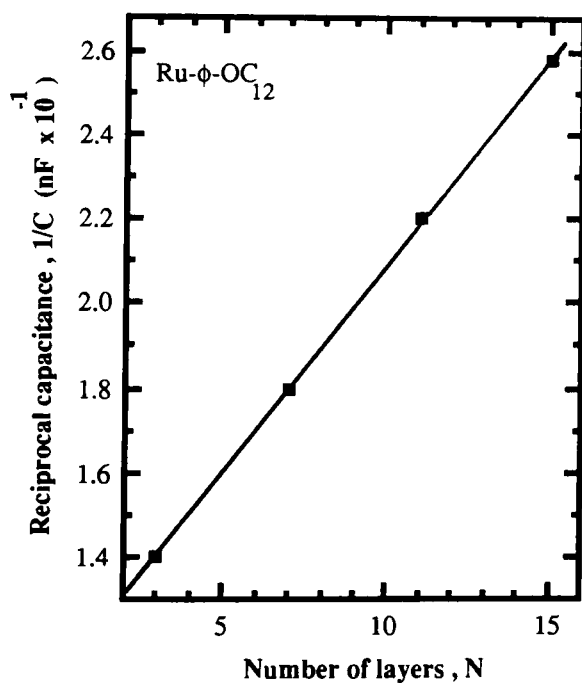
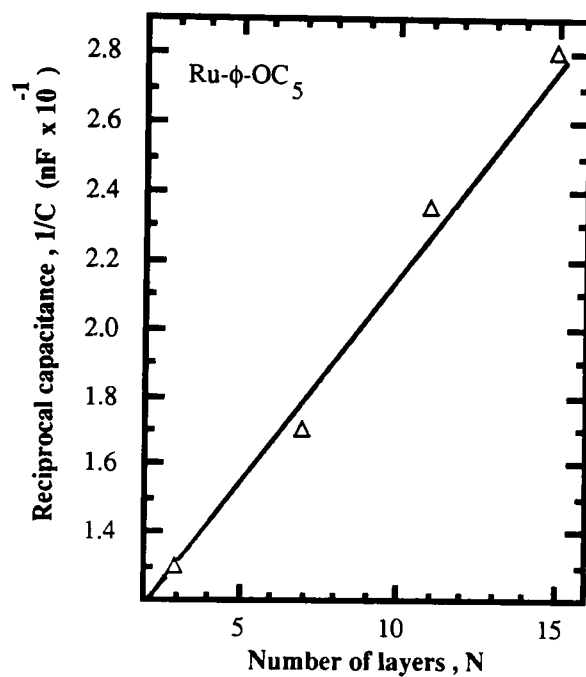
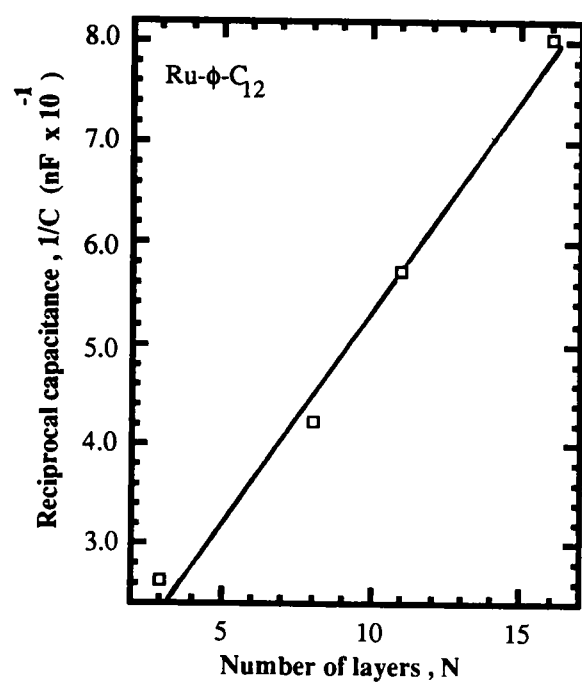


Figure 6.13 : Capacitance characterisation of organo-ruthenium complexes.

Complex	$\frac{d}{\epsilon_r}$ ^{1 MHz} nm	ϵ_r ^{1 MHz}
Ru- ϕ -C ₁₂	0.842	2.87
Ru- ϕ -OC ₅	0.248	5.56
Ru- ϕ -OC ₁₂	0.241	7.63
Ru- ϕ -OC ₁₇	0.232	9.40

Table 6.3 : The dielectric thickness and dielectric constant of several organo-ruthenium complexes in LB film form estimated by measuring the capacitance of MIM (metal - insulating LB film - metal) structures at 1 MHz.

6.5 Thermal stability of organo-ruthenium complexes and their precursors.

In this section, the thermal stability of the bulk powders of the organo-ruthenium complexes and their precursors have been studied. The temperature at which the LB film structure deteriorates has been investigated for the complexes in order to assess the maximum working temperature of a device based upon these materials. The thermal stability has been optimised by modifications to the molecular structure.

6.5.1 Bulk powder thermal properties.

The active material in a practical optical or pyroelectric device may be required to withstand relatively high temperatures. It is therefore important to optimise the thermal stability in order that the efficiency of the device remains little affected over the operating temperature range. The organo-ruthenium complexes and their corresponding precursors exhibit particularly interesting stability properties. The powder melting points of many of the compounds discussed in this thesis are shown in Table 6.4. The most striking feature of these data is that in all cases the melting point of the ruthenium complex is higher than that of the corresponding precursor. This is not surprising as the main intermolecular forces which ultimately determine the melting point are dipole-dipole and van der Waals' interactions and an additional strongly attractive ionic interaction which is, of course, absent from the precursors. Indeed, one of the main reasons for researching organometallic complexes is because of their high thermal stability compared with many other organic materials.

The melting point of the organo-ruthenium complexes appear to be somewhat governed by the length of the substituted alkyl chain. For example, the difference between the melting points of complexes $\text{Ru-}\phi\text{-N}_2^+\text{-}\phi\text{-OH}$ and $\text{Ru-}\phi\text{-N}_2^+\text{-}\phi\text{-OC}_{16}$ is 57°C although the only structural difference is the hexadecyl chain. Therefore, the chain is thought to

Complex	Melting point of precursor T_p °C	Melting point of Ru complex T_{Ru} °C
$Ru-\phi-C_5$	130	131
$Ru-\phi-C_{12}$	-	122
$Ru-\phi-OC_{12}$	91 (70)	122
$Ru-\phi-OC_5$	96	102
$Ru-\phi-OC_{12}$	74	76
$Ru-\phi-OC_{17}$	67	73
$Ru-\phi-C_2''-\phi-OC_{14}$	89	93
$Ru-\phi-C_2''-\phi-OC_{13}$	-	91
$Ru-\phi-N_2''-\phi-OH$	-	147
$Ru-\phi-N_2''-\phi-OC_{16}$	-	90
$Ru-\phi-NH_2$	86	148
$Ru-\phi-NMeC_{17}$	57	86
$Ru-\phi-N_2''-\phi-NMe_2$	179	195
$Ru-\phi-N_2''-\phi-NMeC_7$	78	120

Table 6.4 : Bulk powder melting points of the organo-ruthenium complexes and their precursors.

hinder the packing efficiency of the ruthenium molecules in the crystal lattice as the intermolecular interactions are greatly reduced thus lowering the amount of energy required to melt the solid structure. Figure 6.14 shows the dependence of the melting point of the alkoxy substituted ruthenium complex $\text{Ru-}\phi\text{-OC}_n$ and their precursors on the length of their carbon chain. In the case of the precursors, the melting point gradually rises with chain length. This behaviour is similar to that of the carboxylic acids, also shown in Figure 6.14, and can be attributed to an increase in van der Waals' attractions that occur along the length of adjacent chains. However, the packing in the ruthenium complexes is dominated by the ionic interaction between the ruthenium cationic headgroup and the hexafluorophosphate counter-anion. This interaction is reduced as the chain becomes longer because the molecular packing is disrupted. Thus the melting point of the ruthenium complexes falls due to the resulting decrease in ionic attractions and the corresponding requirement for less energy to melt the solid. Normally, the LB film-forming properties are improved for relatively long chains. However, in this study it has proved possible to produce reproducible multilayer LB films with only a pentyl substitution in order to optimise the thermal stability.

6.5.2 The thermal stability of deposited LB films.

An assessment of the thermal properties of transferred LB films has also been made, the experimental details of which were described in Chapter 4. Heating of the LB layer deposited onto aluminised glass occurs as the optical absorbance of the film is continuously monitored using the MCPD-100 3C spectrophotometer in the reflection geometry. As the temperature increases, changes to the optical absorption are recorded as shown in Figure 6.15a for a 3 layer multilayer of complex $\text{Ru-}\phi\text{-C}_{12}$. Clearly, no appreciable change to the spectrum occurs until 120°C when the intensity of absorption begins to fall dramatically. This decrease can be attributed to the entire structural deterioration of the film. At high temperatures (>140°C) the spectrum is modified by the

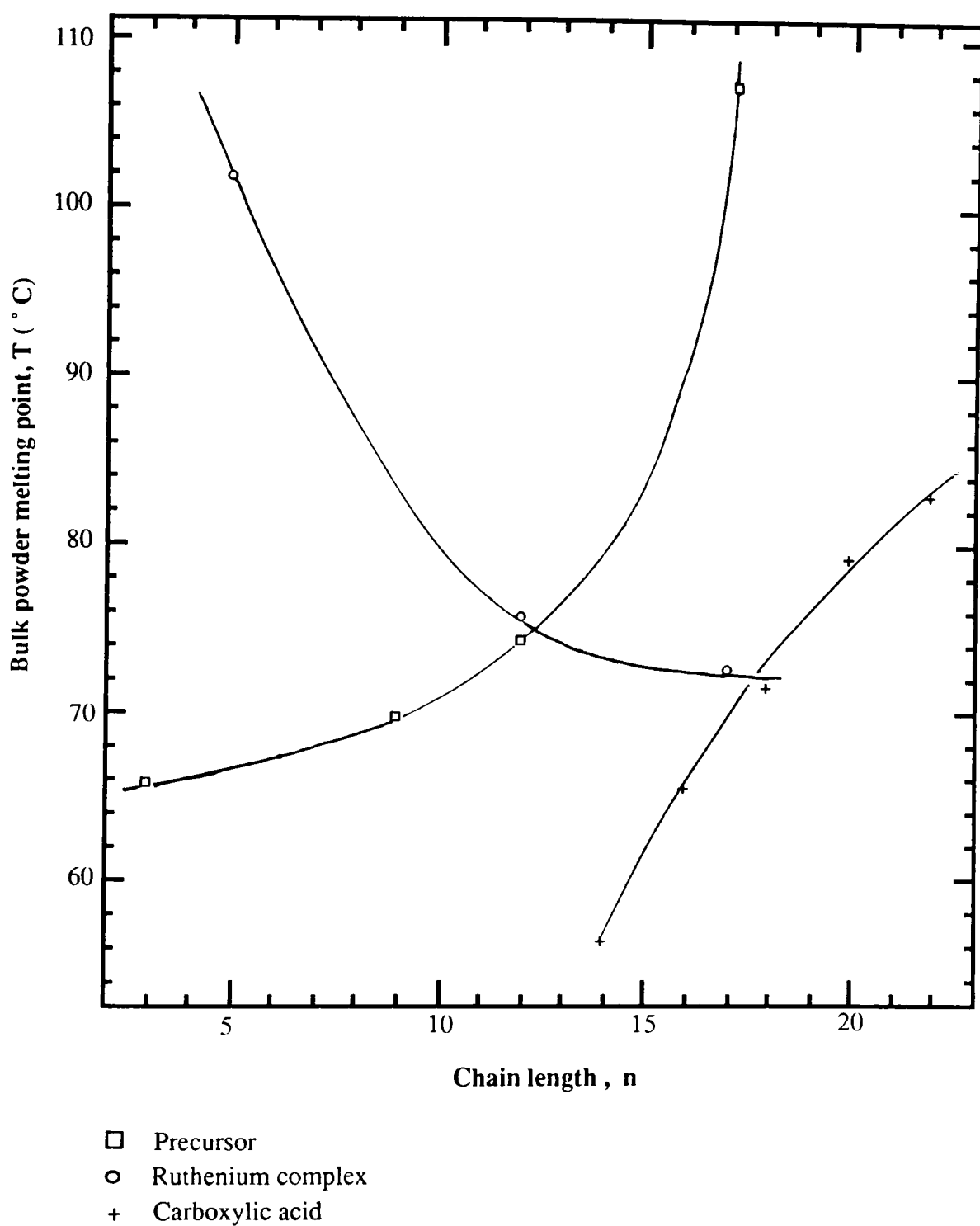


Figure 6.14 : Melting points of bulk powders of organo-ruthenium complexes and their precursors and the carboxylic acids.

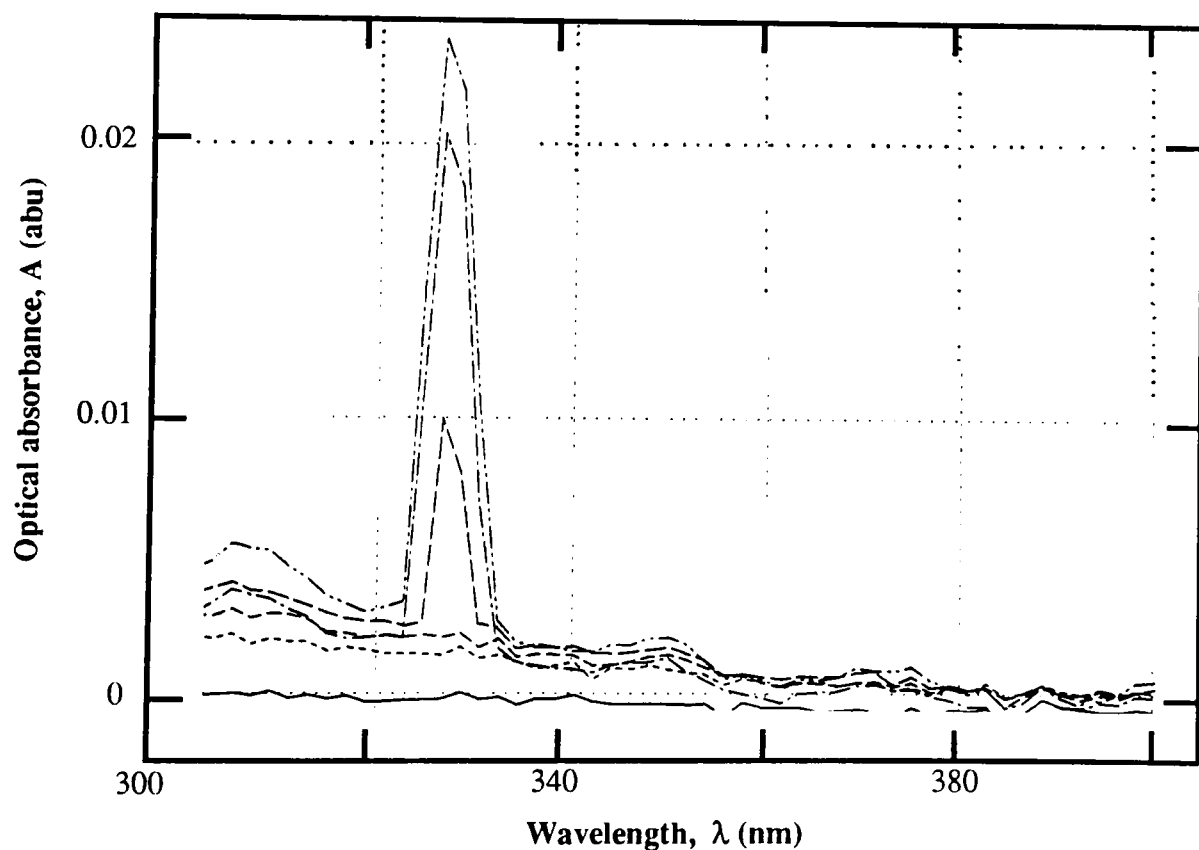
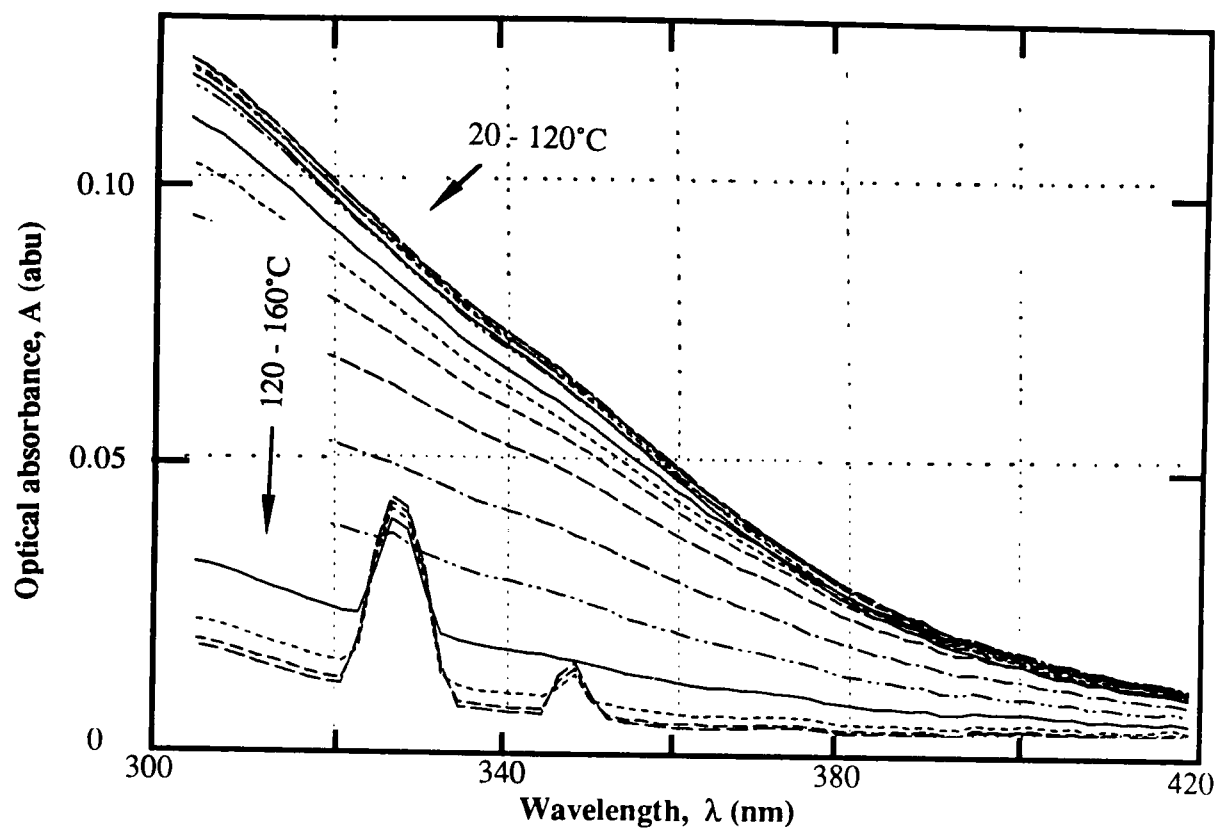


Figure 6.15 : Thermal degradation of organo-ruthenium LB films monitored using uv spectroscopy. (a) Extinction of absorption spectrum as the temperature increases and (b) the effect upon the substrate ($\text{Al}/\text{Al}_2\text{O}_3$).

appearance of a spectral spike at 325nm. A control experiment in which the aluminised substrate with no LB film coating was heated in an identical manner, also led to the observation of this peak as indicated by Figure 6.15b . It must be concluded, therefore, that this feature occurs as a result of the substrate and not because of the LB film. It is interesting to note that the bulk powder melting point of this complex has been measured to be 122°C which is consistent with the breakdown temperature, T_{LB} , of the LB film. However, the T_{LB} value is often higher than the powder melting point as shown in Figure 6.16 in which the normalised peak absorbance is plotted as a function of temperature for the three complexes $Ru-\phi-OC_n$ with $n=5, 12$ and 17 . The behaviour of complexes $Ru-\phi-OC_5$ and $Ru-\phi-OC_{12}$ is similar with an initially constant peak absorbance followed by a dramatic fall as the film melts. For $Ru-\phi-OC_5$ the T_{LB} breakdown point is 100°C compared to an identical powder melting point and for $Ru-\phi-OC_{12}$, T_{LB} is again 100°C although the powder melting point is only 74°C. The behaviour of the $Ru-\phi-OC_{17}$ LB film is different to the $n=5$ and $n=12$ derivatives. In this case, the absorbance rises gradually in the region $45^\circ C < T < 70^\circ C$, saturates and is preceded by the usual decrease as melting occurs. The change in absorbance in this temperature region is reversible and is believed to occur as a result of a molecular re-ordering process although no detailed investigation has yet been performed. The T_{LB} value for $Ru-\phi-OC_{17}$ is 80°C compared with a powder value of 71°C.

It is interesting to notice that the complex $Ru-\phi-OC_{17}$ which displays this unusual behaviour is also the compound which exhibits the largest pyroelectric response which will be discussed in detail in Chapter 7. The possible reorganisation of the molecules in the above-mentioned temperature range may lead to a large polarisation change and thus a large pyroelectric current.

Summarising, the thermal stability properties of many of the ruthenium complexes and their precursors have been studied. The bulk powder and the LB film melting points

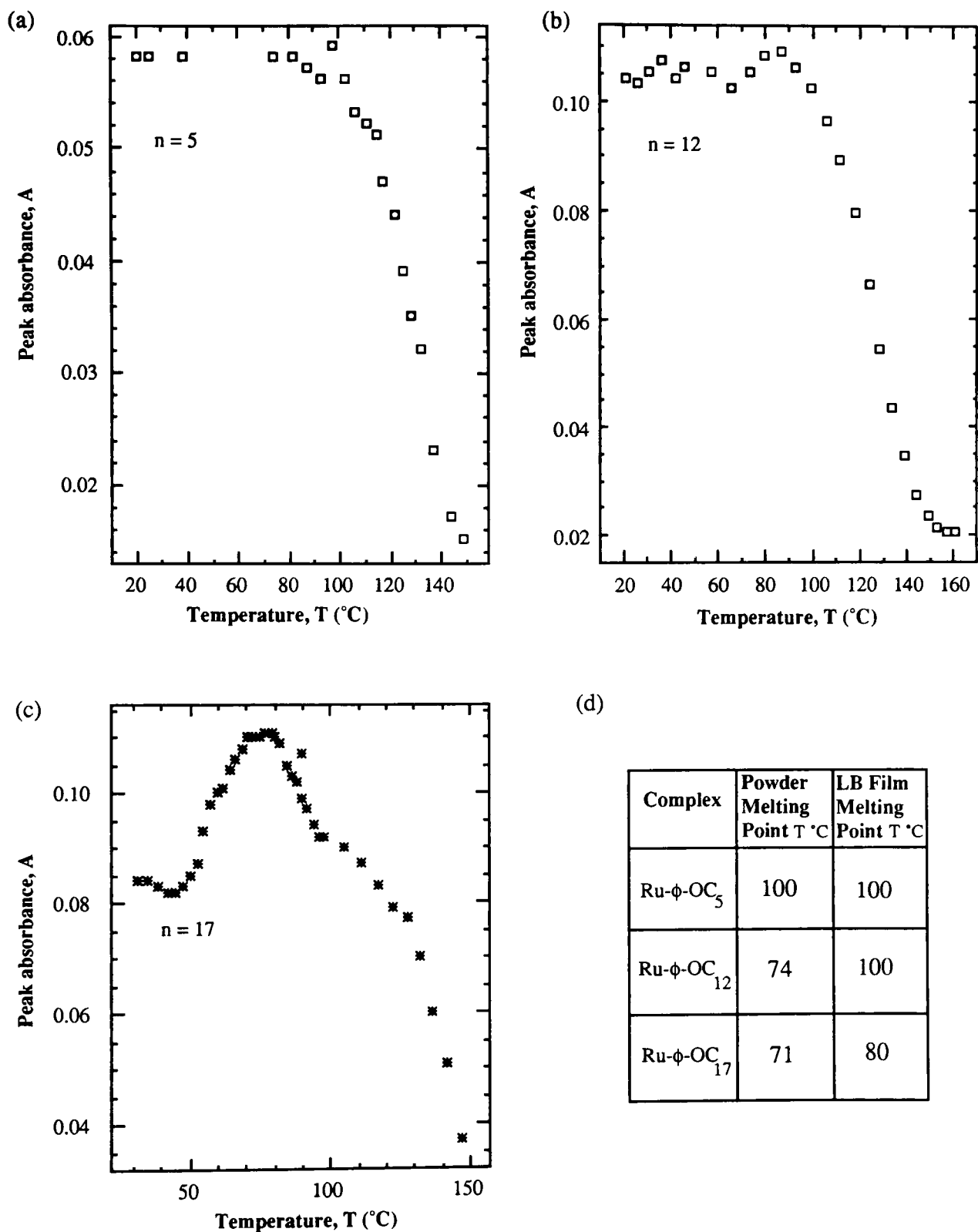


Figure 6.16 : Breakdown temperature profiles for $\text{Ru-}\phi\text{-OC}_n$ multilayer films. (a) $\text{Ru-}\phi\text{-OC}_5$, (b) $\text{Ru-}\phi\text{-OC}_{12}$ and (c) $\text{Ru-}\phi\text{-OC}_{17}$. The melting temperatures are shown in the table (d).

have been optimised in the case of the $\text{Ru-}\phi\text{-OC}_n$ complexes by reducing the length of the substituted carbon chain.

6.6 Structural studies.

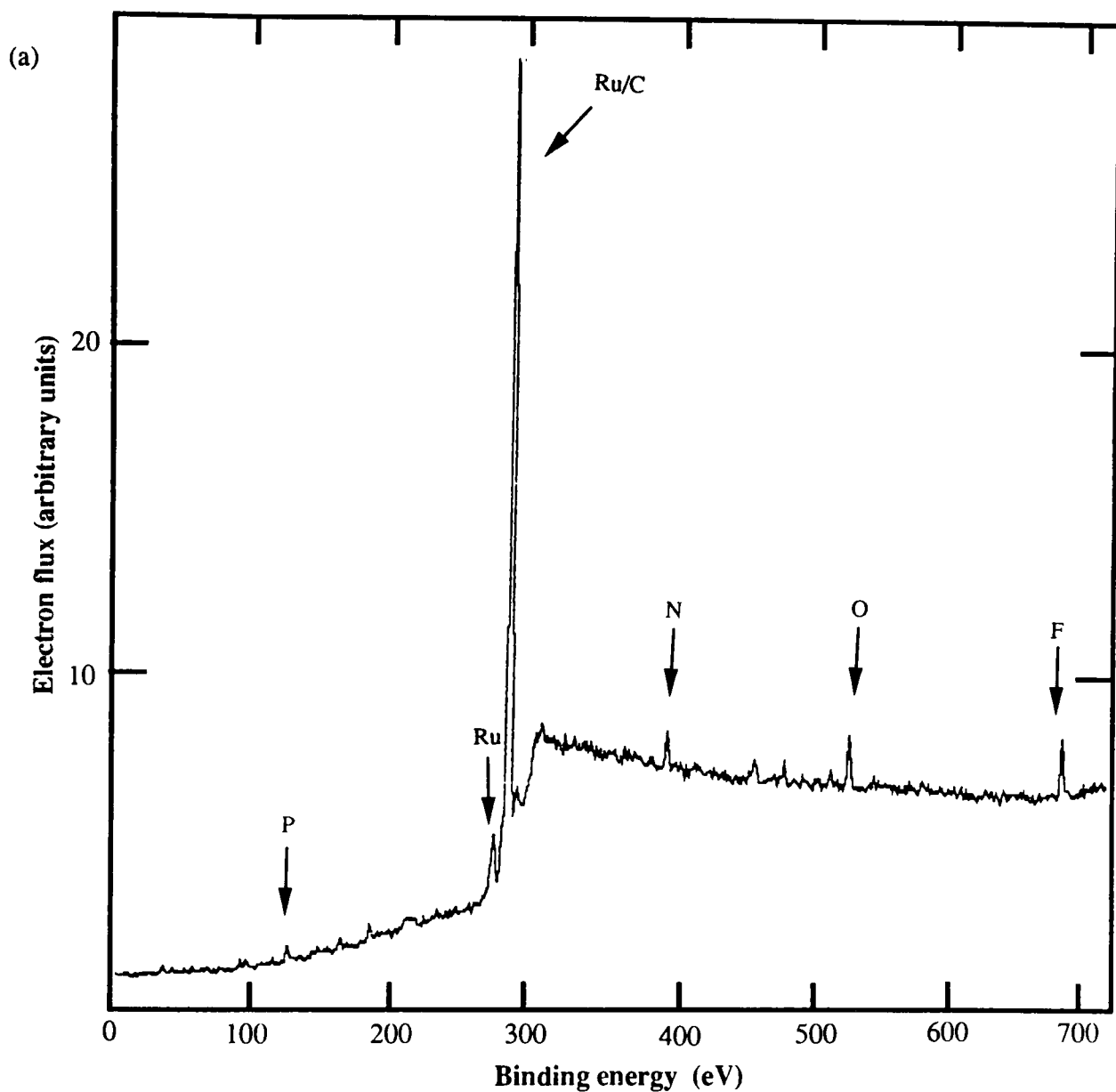
This section is involved with the structural assessment of LB films of the ruthenium complexes. Three techniques have been used: namely ESCA, scanning optical microscopy and transmission electron diffraction which have been briefly described in Chapter 4.

6.6.1 Electron spectroscopy.

ESCA is concerned with the measurement of core electron binding energies. A molecule is bombarded with a source of high-energy X-rays which cause the emission of inner-shell electrons from its constituent atoms. All electrons whose binding energies are less than the energy of the exciting X-rays are ejected, and their energy is measured by an energy analyser. Binding energies unambiguously define a specific atom and can effectively produce a "fingerprint" of the molecular compound under investigation rather like infra-red spectroscopy.

The X-ray photons can penetrate the organic material to a considerable depth (around 1-500nm). However, only the electrons emitted from atoms near to the surface (usually within 5nm of the surface) have any chance to escape the bulk and be detected. The technique thus provides elemental analysis data for very thin surface layers of material and is, therefore, ideally suited to the study of LB films.

Figure 6.17 shows the energy spectrum in the range 0–750 eV for an 11 layer sample of complex $\text{Ru-}\phi_3\text{-C}_5$. Clearly, the electron flux shows large peaks at well-defined



(b)

Atom	Electron	Energy (eV)
Ru	4P3	45
	3D5	282
	3D3	286
	3P3	463
	3P1	485
C	1S	287
O	1S	531
F	1S	686
P	2P3	133
N	1S	402

(c)

Atom	Abundance wrt Ru	Expected ratio
Ru	1.0	1
C	160.577	65
O	1.2	0
F	5.287	6
P	4.319	3
N	2.424	1

Figure 6.17 : ESCA characterisation of $\text{Ru-}\phi_3\text{C}_5$ LB films. (a) The binding energy profile showing the peaks corresponding to inner-core electrons, (b) the binding energies of electrons expected to be present and (c) the abundance ratios (relative to Ru) of the electrons found.

energies which correspond to matching of the X-ray photon energy with the binding energy of particular core electrons. In practice, certain energy ranges are studied in extreme detail to unambiguously determine the position of the peaks. Figure 6.17b shows the binding energies of the electrons from the atoms expected to be present in the film in order to determine the elemental constitution of the compound. The data in Figure 6.17c indicate the relative abundance of each element normalised with respect to the ruthenium peak. The expected ratios are also shown. The agreement, although moderate, is not sufficiently precise to enable the technique to be used for accurate quantitative analysis. However, ESCA is invaluable for qualitative determination of the presence of certain elements.

In summary, the ESCA technique is useful for qualitative surface studies of thin LB layers and provides information regarding the abundance of particular elements within organic molecules.

6.6.2 Scanning optical microscopy.

Scanning optical microscopy provides a means of imaging microstructures with higher resolution than can be obtained using conventional light microscopy. The technique has been briefly used in the course of this work to assess the feasibility of its use in studying the structural quality of LB film samples and in particular to show the improvement in quality of the organo-ruthenium monolayers when compared, where possible, to those of the precursor molecules.

Figure 6.18 shows three images obtained using a Lasertec Corporation Scanning Laser Microscope 1LM11. Figure 6.18a is a photograph of a clean, uncoated aluminised glass substrate showing very few surface features. The photograph in Figure 6.18b shows the enormous number of surface inhomogeneities in the monolayer of the precursor NC-

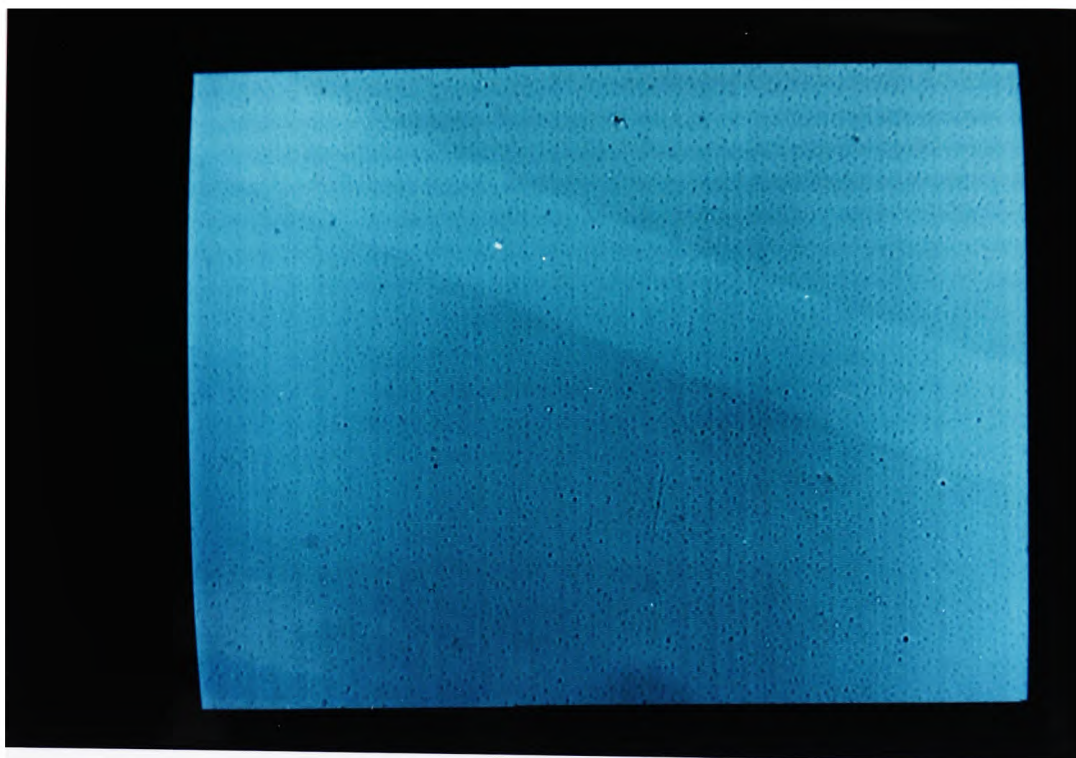


Figure 6.18a : An SOM image of a cleaned aluminised glass substrate.

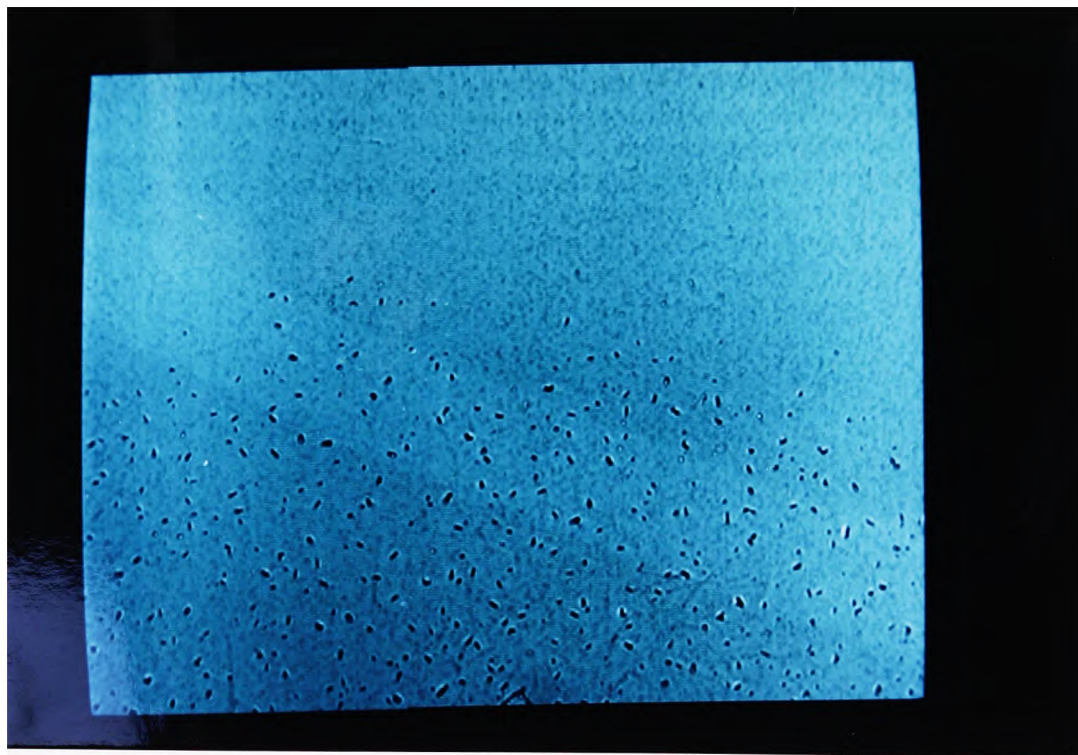


Figure 6.18b : An SOM image of the above substrate coated with a monolayer of the precursor $\text{NC-}\phi_3\text{C}_5$.

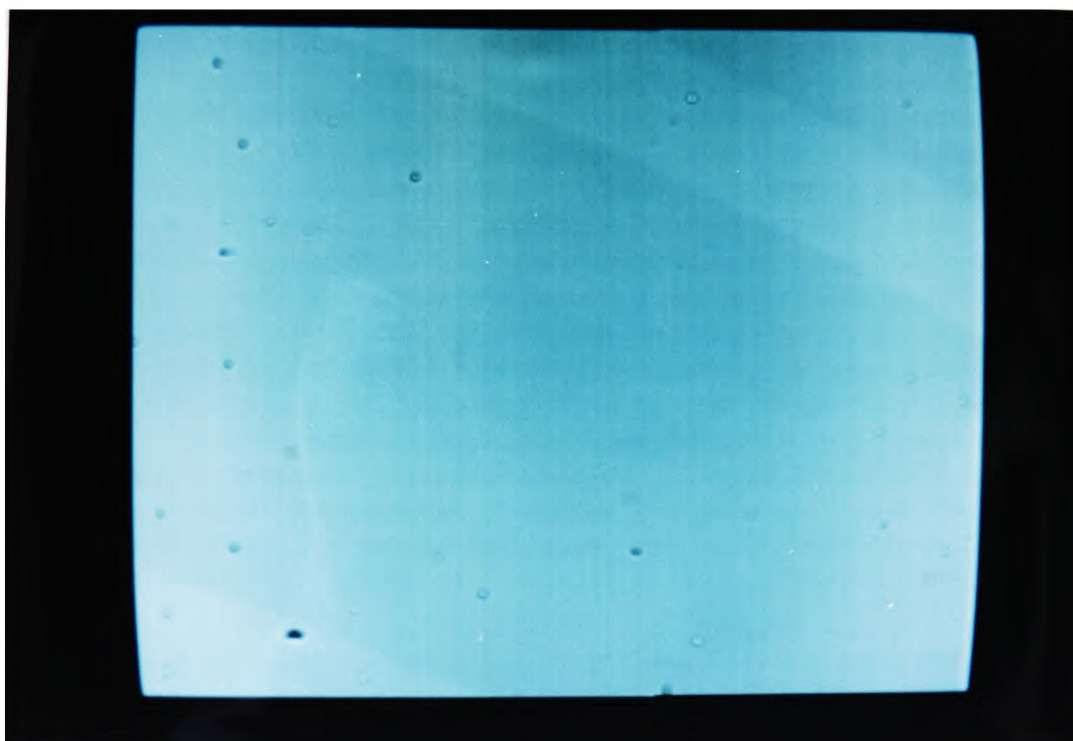


Figure 6.18c : An SOM image of a monolayer of complex $\text{Ru-}\phi_3\text{C}_5$ on an alumined glass substrate.

ϕ_3 -C₅. The film appears to be composed of many crystallites distributed randomly over the substrate surface. Finally, Figure 6.18c presents an image of a Ru- ϕ_3 -C₅ monolayer in which far fewer surface artefacts are visible. It can be concluded that the adoption of the ruthenium headgroup has greatly improved the quality of the LB monolayer. It is hoped that the SOM facility will be used extensively in the future for structural analysis of LB structures in order to minimise the number of surface defects.

6.6.3 Transmission electron diffraction.

The TED technique was discussed in Chapter 4. Its major disadvantage is that the electron beam is damaging to many organic materials and usually a diffraction pattern may only be observed for a few seconds. However, by skilfully optimising the beam energy and the exposure time, it has been shown by Mr. D. Heard [112] of the Molecular Electronics Group that useful diffraction images can be obtained.

Figure 6.19 displays a photograph of a pattern obtained from an 11 layer LB film of complex Ru- ϕ -OC₅. The rings are not sharp indicating that the molecular lattice sites are not precisely defined although reasonable order is found in a polycrystalline film. The position of the ring implies a d-spacing of 0.35 nm. Further work is being performed in order to establish the variation in lattice parameters as a function of chain length and the different functional groups present within the ruthenium complexes.

Most of the TED studies on LB films in the past [113] have centred on the well-behaved fatty acid molecules. The concurrent systematic study of ruthenium complexes should yield useful information regarding the relationship between crystalline order and molecular structure for more useful materials which are envisaged to form the active component of novel devices.



Figure 6.19 : An electron diffraction pattern obtained from an 11 layer LB film of complex Ru- ϕ -OC₅.

6.7 Summary.

This chapter has been concerned with the characterisation of LB films of organo-ruthenium complexes using several techniques. The deposition conditions have been optimised and the resulting LB film optical absorption spectra have been recorded and compared to the solution and Langmuir film values. The importance of considering optical interference effects when measuring absorption has been stressed. The thickness and refractive index of LB films have also been measured using ellipsometry and the surface plasmon resonance techniques with excellent mutual agreement.

The quartz microgravimetric technique has enabled the deposition of organo-ruthenium monolayers to be further characterised. It has proved to be extremely sensitive by demonstrating the ability to resolve complexes of different molecular weights and detect the mass change associated with intra-lattice incorporation of precursor molecules. The capacitance of MIM (metal-insulator-metal) structures, with the ruthenium multilayer behaving as the insulator, has enabled the dielectric thickness and dielectric constant (1MHz) to be estimated. The thermal stability of the organometallic complexes and their corresponding precursors in powder and LB film form has been studied and optimised for the system $\text{Ru-}\phi\text{-OC}_n$. Finally, the techniques of ESCA, SOM and TED have been used to begin an investigation into the structural properties of LB films of the ruthenium complexes.

CHAPTER 7

Non-linear Physical Properties of Organo-Ruthenium Complexes and their Precursors.

7.1 Introduction.

Many of the ruthenium complexes and precursors that have been discussed in this thesis possess electron donating and withdrawing groups separated by a region of extensive electronic conjugation. These properties lead to the presence of a highly polarisable region of electron density and a large dipole moments. Such characteristics are essential for the observation of second-order physical effects such as optical second-harmonic generation (OSHG), pyroelectricity and piezoelectricity. However, a vital additional requirement must also be satisfied. The individual molecules must be arranged in a non-centrosymmetric manner [114] such that a macroscopic polarisation exists in the bulk material. Many organic molecules exist (including the majority of those studied in this work) which possess these necessary molecular characteristics although their symmetrical configuration within the crystal lattice prevents the observation of second-order effects.

Several techniques are available that provide a means of inducing partial alignment of the asymmetric molecules to allow the molecular non-linearities to be exposed and

measured. These include guest-host polymer spinning (followed by electrical poling), LB film deposition and the electric-field induced alignment of molecules in solution. EFISHG, described in detail in Chapter 4, has been used extensively in this work to measure the optical non-linearities of the nitrile-terminated precursor molecules and the results are discussed in section 7.2 . The non-linear optical properties of LB films are presented and the problems associated with these measurements are explained. Finally, the pyroelectric properties of some of the ruthenium complexes are discussed.

7.2 Non-linear optical properties of the nitrile precursors.

7.2.1 Introduction.

In this section, the detailed investigation of the non-linear optics of the precursors using EFISHG is described and the magnitude of the response is related to their molecular structure. Most of the non-linear optics work has concentrated upon measuring the non-linearities of the free molecules in solution in order to establish the intricate relationship between the amplitude of the response and the chemical structure with no significantly large, perturbing dipole-dipole interactions which would be present in the solid phase. The sample solution must be able to sustain a large electric field (kVcm^{-1}) and, as a result, the technique is only useful for non-ionic compounds. Therefore, the ruthenium complexes themselves cannot be studied in this manner. However, in the case of the complexes, each precursor is chemically bonded to the same ruthenium headgroup and therefore the substitution is envisaged to produce a similar effect upon the second-order non-linearity of each precursor. A study of the precursors therefore yields much useful data concerning the expected behaviour of the aligned ruthenium molecules.

The *detailed* experimental results of only a few of the precursors investigated are described, although the measured values of the important parameters, including the

second-order non-linear optical hyperpolarisability, β , are presented for all of the compounds studied. The units used are discussed in Appendix B.

7.2.2 Measurement of the second-harmonic generation from precursor solutions.

In order to estimate the second-order non-linear optical hyperpolarisability of a compound using the EFISHG technique, the product must be dissolved in a solvent whose optical characteristics are themselves well-known. Acetone is used where possible as its non-linear properties have been accurately measured. The magnitude of the second-order optical response should increase as the concentration of the solution increases and, for this reason, several solutions of different concentration are studied in order to obtain a mean value of the optical coefficients.

The solution is placed into a cell in which two optical windows form a wedge-shaped test region (see section 4.4.2). The cell is translated across the incident YAG laser beam such that the path length in the solution gradually increases. The second-harmonic output intensity detected by the photomultiplier rises and falls periodically as the path length encompasses integer numbers of coherence lengths. The coherence length is therefore the maximum usable thickness from which the largest attainable second-harmonic output is generated. From simple geometry, the displacement of the solution cell across the beam which corresponds to a change in the path length of one coherence length is given by:

$$l_c = \frac{1}{2} \delta_{if} \tan \alpha \quad (7.1)$$

where δ_{if} = the displacement of the cell across the YAG beam, l_c = the coherence length and α = the wedge angle. For acetone $l_c = 26.0 \mu\text{m}$ and δ_{if} in this experiment is equal to

0.96mm. This corresponds to a wedge angle of 3.1° . The cell is now calibrated and may be used to measure the non-linearity of the precursor. It is interesting, however, to observe the relationship between the coherence length and the solution concentration. Figure 7.1 shows this behaviour for compounds NC- ϕ_2 -C₁₁, NC- ϕ_3 -C₅ and NC- ϕ -C₂"'- ϕ -OC₁₄. The change in coherence length as the concentration increases is attributed to the change in the refractive index and the dispersion relation of the solution. The difference in propagation conditions for beams at ω and 2ω determine their phase relationship and therefore the interference properties. Therefore the change in coherence length is a manifestation of the alteration to the dispersion relation caused by increasing the solution concentration.

Normally, at least three solution concentrations are used. The most dilute is tested first so that slightly improper cleaning of the cell leads to only minor errors. In all cases except for the azobenzene compounds, a YAG laser output at $1.06\mu\text{m}$ was used as the fundamental exciting wave and no or very little absorption was observed at either the fundamental (ω) or the second-harmonic (2ω) frequency. The azobenzene derivatives were measured using $1.34\mu\text{m}$ radiation from a YAG laser so that again the absorption at ω or 2ω was insignificant.

Figure 7.2 shows the variation in the peak-peak amplitude of the second-harmonic output of three solutions of compound NC- ϕ_3 -C₅. Clearly, a greater response is observed as the concentration increases as expected. Each data point corresponds to the average of three separate scans using each concentration. The ratio of the second-harmonic intensity of the solution to that obtained from acetone alone eventually yields the non-linearity of the solute molecules. Equation 4.7 (shown below for clarity) relates the third-order macroscopic susceptibility $\Gamma_{nl}(x)$ to the ratio of the second-harmonic intensity of the solution to that of acetone:

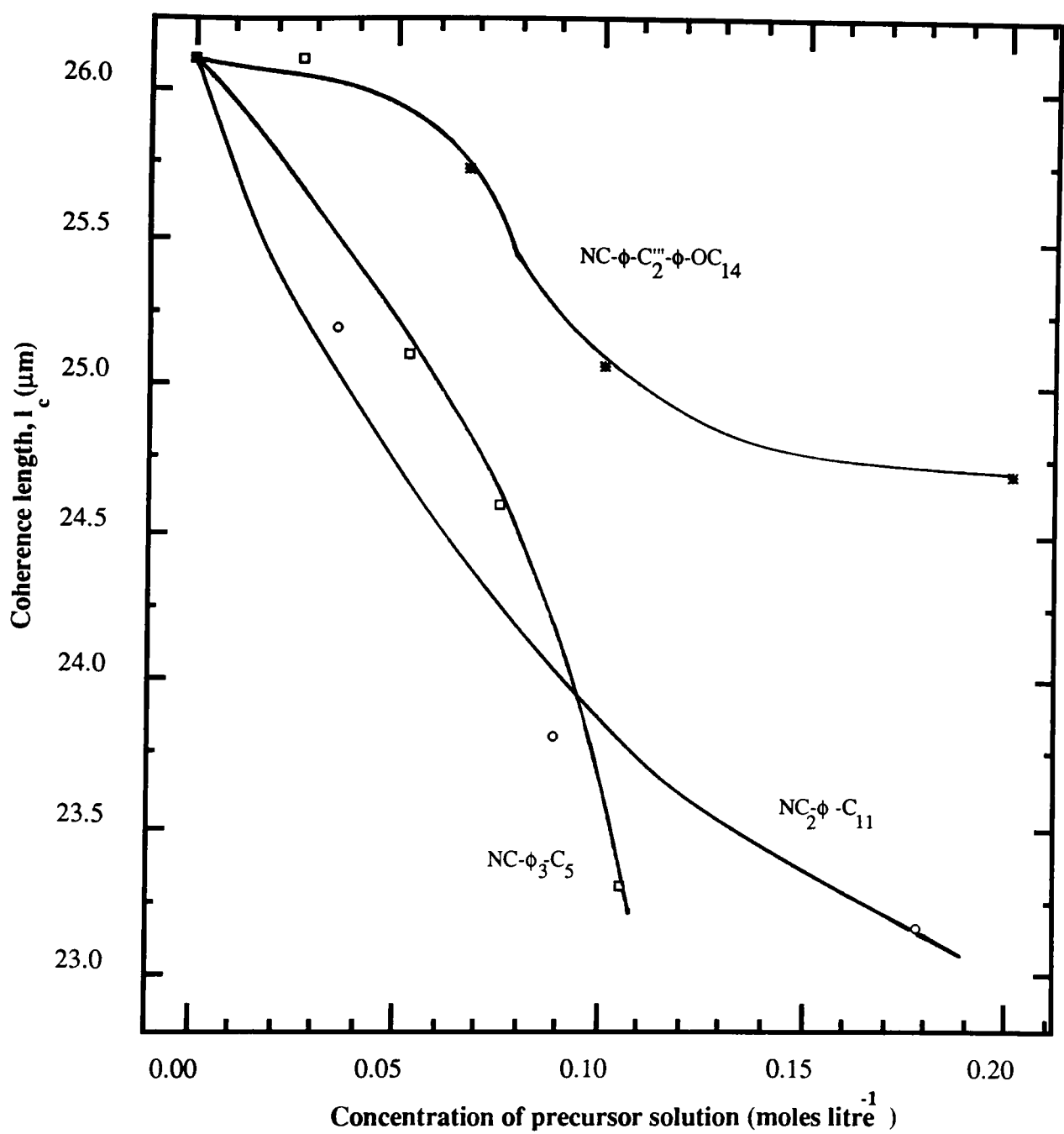


Figure 7.1 : The variation in coherence length as a function of the concentration of the precursor solution (acetone).

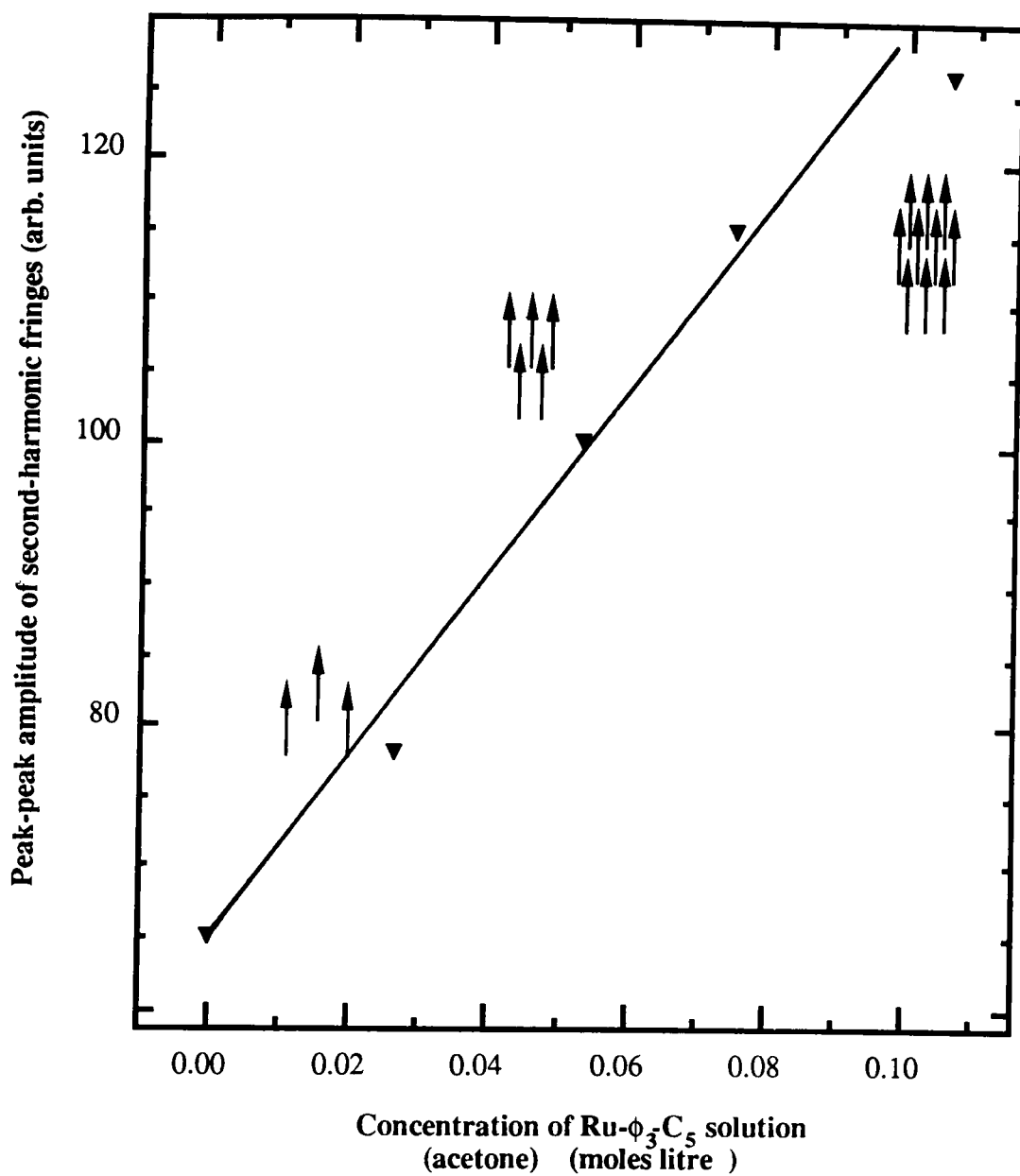


Figure 7.2 : The relationship between the amplitude of the second-harmonic fringes obtained from a solution of Ru- ϕ_3C_5 and the solution concentration. The arrows signify the solute molecules.

$$\Gamma_{nl}(x) = \frac{1}{I_c(x)} \left\{ 1.51 \left(\frac{I_{nl}^{1/2}(x) V_s}{I_s V_{nl}} \right) 10^{(\frac{\rho}{2})} + 0.62 \right\} \quad (7.2)$$

where the symbols are described in Chapter 4.

The plot in Figure 7.3 shows the variation in $\Gamma_{nl}(x)$ as a function of concentration for the two compounds NC- ϕ -C₂^{'''}- ϕ -OC₁₄ and NC- ϕ -C₅ showing a linear relationship as expected from equation 4.9. Using the values of $\Gamma_{nl}(x)$ the third-order hyperpolarisabilities γ_{nl} may be calculated from this same equation and finally a value for the product $\mu\beta$, where μ = the dipole moment and β = the second-order non-linear optical hyperpolarisability, can be found using equations 4.9 and 4.10.

Table 7.1 lists the values of $\Gamma_{nl}(x)$, γ_{nl} , $\mu\beta$ and β for all the precursors tested. Also, the value of β_0 , the off-resonance coefficient, is given. These data are explained in the following sections.

7.2.3 Analysis of the hyperpolarisability of the precursors.

Table 7.1 shows the non-linear optical coefficients of all the nitrile precursor compounds studied in this work. The aim of this section is to explain the non-linear response in terms of the detailed molecular structure of the materials. The strength of the electron donating groups and the type and extent of the electronic conjugation have been found to have a dramatic effect upon β .

(i) The effect of electron donation on the second-order non-linear optical response.

In order to describe the effect of different electron donor groups on the second-order molecular non-linearity, the single benzene ring system has been chosen. In all

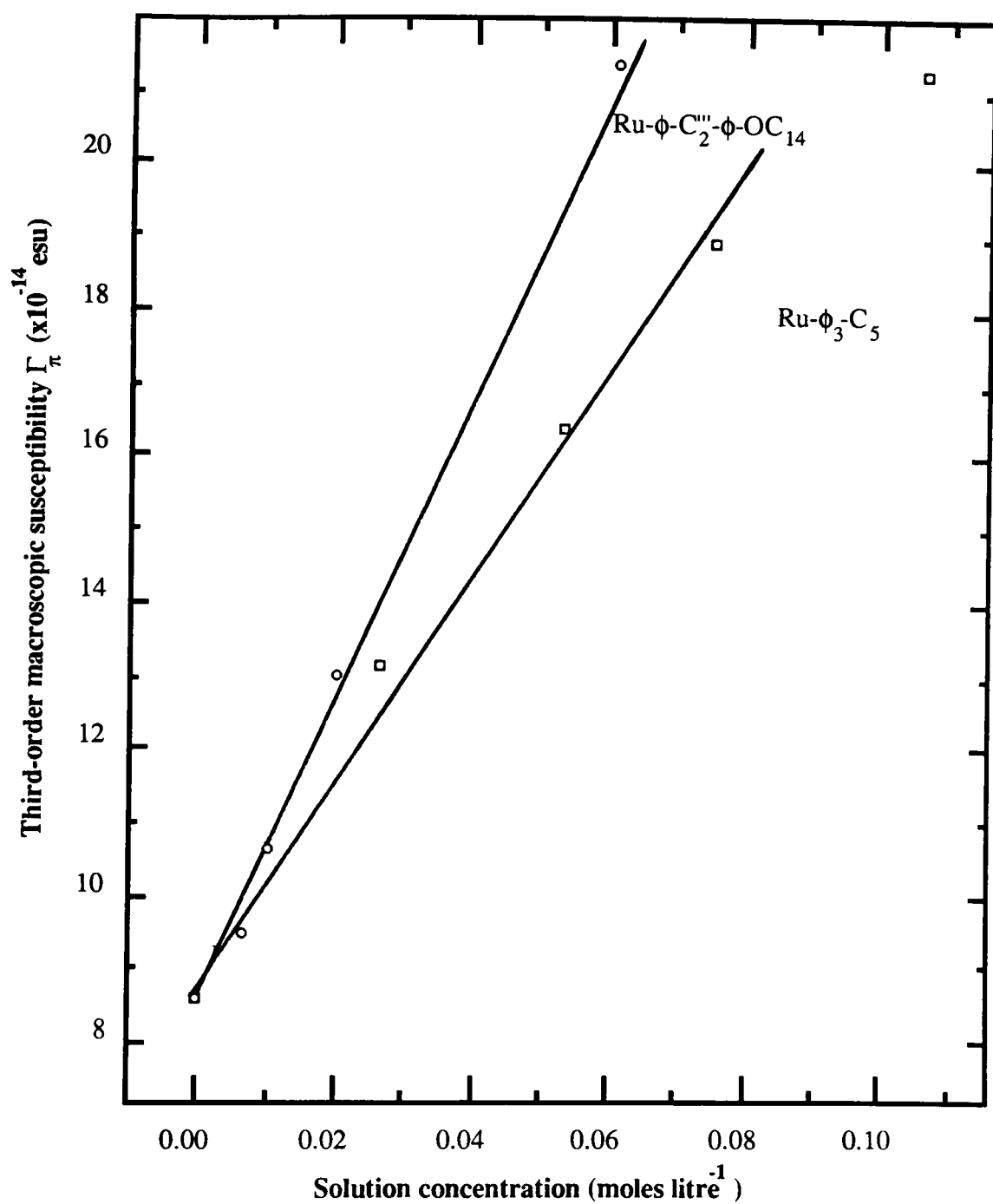


Figure 7.3 : Variation in the thrid-order macroscopic susceptibility as a function of solution concentration for two precursors.

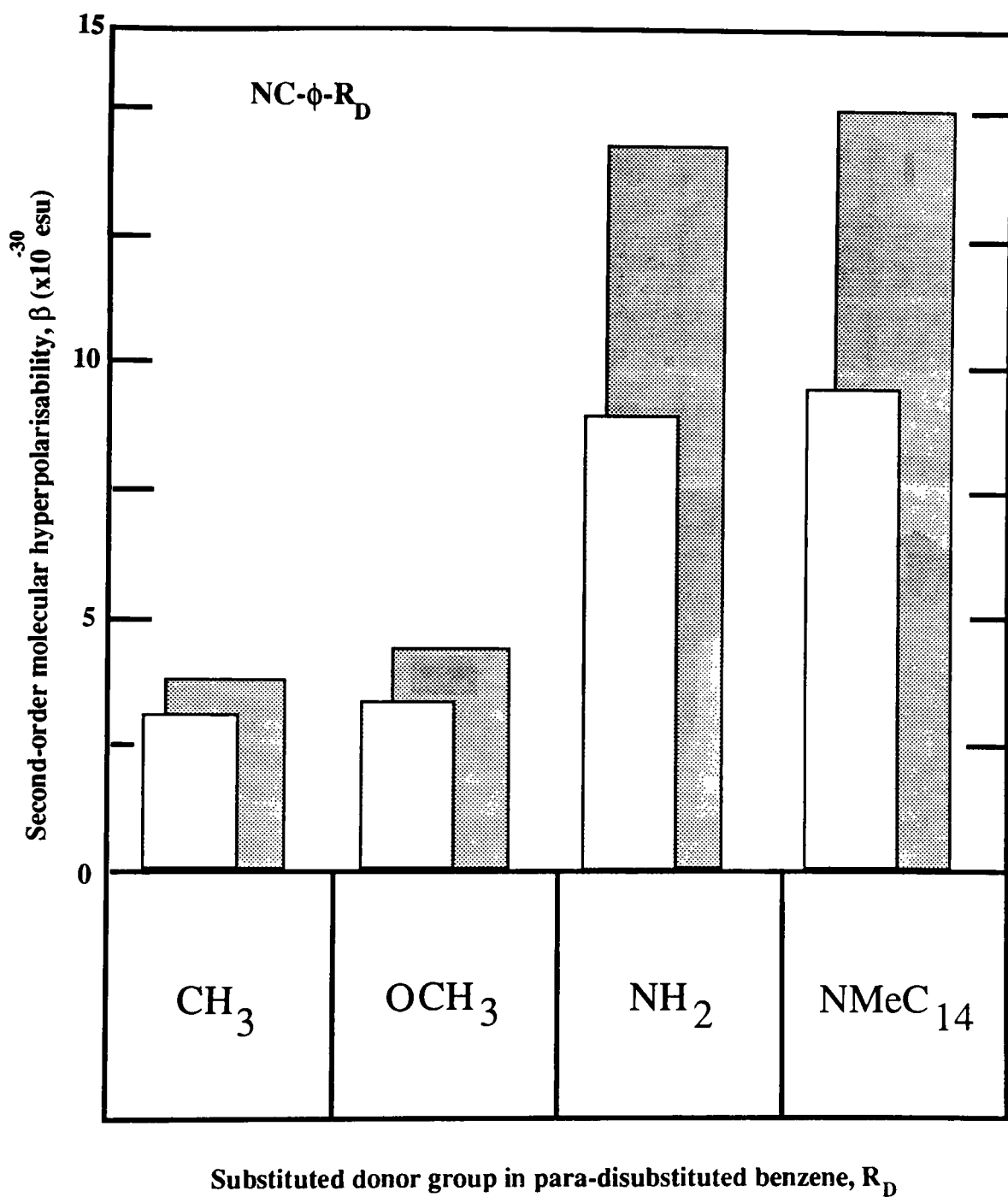
Precursor	$\lambda_{\text{max}}^{\text{soln}}$ nm	γ_{π} $\times 10^{-34}$ esu	$\mu\beta$ $\times 10^{-48}$ esu	μ D	β $\times 10^{-30}$ esu	β_0 $\times 10^{-30}$ esu
NC- ϕ -C ₁	-	0.62	12.8	4.4	2.9	-
NC- ϕ_2 -C ₁₁	-	2.93	60.7	4.0	15.2	
NC- ϕ_3 -C ₅	303	6.9	142.9	6.0	23.8	14.8
NC- ϕ -OC ₃	247	0.93	19.3	5.5	3.5	2.6
NC- ϕ_2 -OC ₁₂	292	5.31	110.0	5.5	20.0	12.9
NC- ϕ -NH ₂	297	2.74	56.7	5.0	11.3	7.2
NC- ϕ -NMeC ₁₄	300	3.82	79.2	6.6	12.0	7.5
NC- ϕ -C ₂ ^{'''} - ϕ -OC ₁₄	321	6.13	127.0	5.0	25.4	14.7
NC- ϕ -C ₂ ^{''} - ϕ -OC ₁₃	344	8.93	185.0	5.0	37.0	19.3
NC- ϕ -N ₂ ^{''} - ϕ -OH [*]	367	33.83	700.6	6.2	113.0	73.2
NC- ϕ -N ₂ ^{''} - ϕ -NMe ₂ [*]	451	49.67	1028.6	7.4	139.0	67.4

Measured at a fundamental wavelength of 1.34 μ m.

Table 7.1 : The non-linear optical coefficients of the precursor compounds showing the relationship between the non-linear response and the molecular structure.

cases, the acceptor is a cyano group. Although it is possible to obtain much stronger electron withdrawal using other groups such as nitro or pyridinium ion moieties, the complexation reaction to form the ruthenium compounds necessitates that the precursor must be nitrile-terminated. Figure 7.4 pictorially shows the value of hyperpolarisability, β , (and the off-resonance value β_0 which will be discussed in section 7.2.2 (iv)) for various electron donor groups, R_D , in the general sub-class NC- ϕ - R_D .

Clearly, the non-linearity increases in the order $\text{CH}_3 < \text{OCH}_3 < \text{NH}_2 < \text{NMeC}_{14}$ which is consistent with the corresponding increase in the strength of the electron donation induced by these groups. Electron injection leads to increased ground state and excited state dipole moments and a lower electronic transition energy. The increase in non-linearity of the NC- ϕ - NH_2 and NC- ϕ - NMeC_{14} precursors compared to the NC- ϕ - CH_3 or NC- ϕ - OC_3 molecules therefore confirms that the change in dipole moment that occurs between the ground and excited states is greatly increased. This is brought about via an intramolecular charge transfer interaction between the donor and acceptor groups. Figure 7.5 shows how the second-order response arises in the NC- ϕ - NH_2 molecule. The incident optical field induces a redistribution of electric charge along the charge-transfer axis of the molecule. However, the resulting change in the polarisation is non-linear. When a large positive field appears along the molecule (case (a) in Figure 7.5) the π -electron density associated with the phenyl ring is redistributed toward the cyano group such that an increased dipole is induced (μ_1). Upon reversal of the field, however, the distribution cannot occur as extensively because of the opposition to charge flow in this direction from the electron donor and acceptor groups. The resulting dipole moment change from the equilibrium value (that occurs at zero field shown in case (b)) is therefore smaller than the change $\mu_1 - \mu_g$. It was explained in Chapter 3 that such a non-linear polarisation response results in the generation of a second-harmonic frequency component.



 β_0
 β

Figure 7.4 : The dependence of the second-order non-linear optical molecular hyperpolarisability upon the strength of the electron donor group, R_D, for four monophenyl precursors.

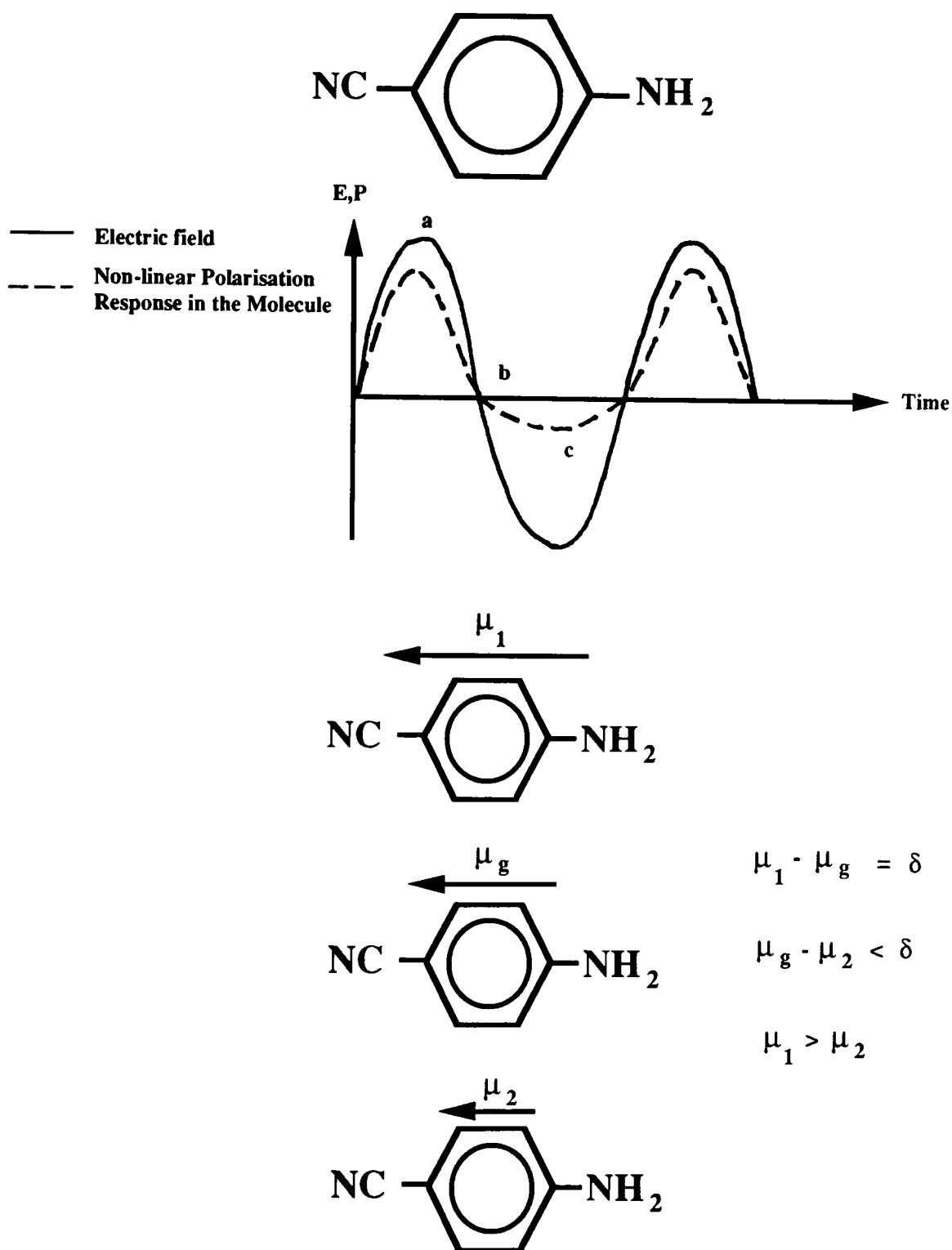


Figure 7.5 : A model to show the origin of the molecular non-linearity in para-disubstitutedbenzene charge-transfer compounds.

It must be mentioned that the second-order optical hyperpolarisability is dependent also upon the optical transition energy and its accompanying oscillator strength. Although the model presented above is simple in nature, it describes effectively the origin of the molecular non-linearities and the need for a strong electron donating group coupled to a region of extensive electronic conjugation.

(ii) The effect of conjugation on the second-order non-linear optical properties: the polyphenyl precursors.

Conjugated electron systems provide a source of highly polarisable π -electrons which may be drastically influenced by substituted chemical groups. Several of the precursors studied in this work consist of two or more directly bonded phenyl rings such as the biphenyl and terphenyl compounds NC- ϕ_2 -OC₁₂ and NC- ϕ_3 -C₅. Their molecular hyperpolarisability has been studied as a function of the number of rings and the resultant effect can be seen from Figure 7.6 . Clearly, β increases dramatically for both systems NC- ϕ_n -C_x and NC- ϕ_n -OC_x in which n is the number of rings and x is the number of carbon atoms in the hydrocarbon chain. It was stressed in Chapter 3 that the charge-transfer contribution to the hyperpolarisability (β_{CT}) is dominant and is proportional to the change in dipole moments of the ground and the primary excited state. The polarisable electron density increases as the number of phenyl rings (the source of π -electrons) increases and, therefore, much larger ground state dipole moments are usually observed. The excited state dipole is correspondingly much larger such that the difference $\mu_e - \mu_g$ itself increases as the number of rings increases. The electron donor in the case of the NC- ϕ_n -C_x precursor is only an extremely weak alkyl group. It is thought that the hyperpolarisability would remain unaffected by alterations to its length and therefore the observed variation in β can be attributed almost entirely to the increase in polarisable π -electrons as n increases. The NC- ϕ_n -OC_x system is an alkoxy chain which is again relatively weak when compared to the amine group, as discussed in the previous section,

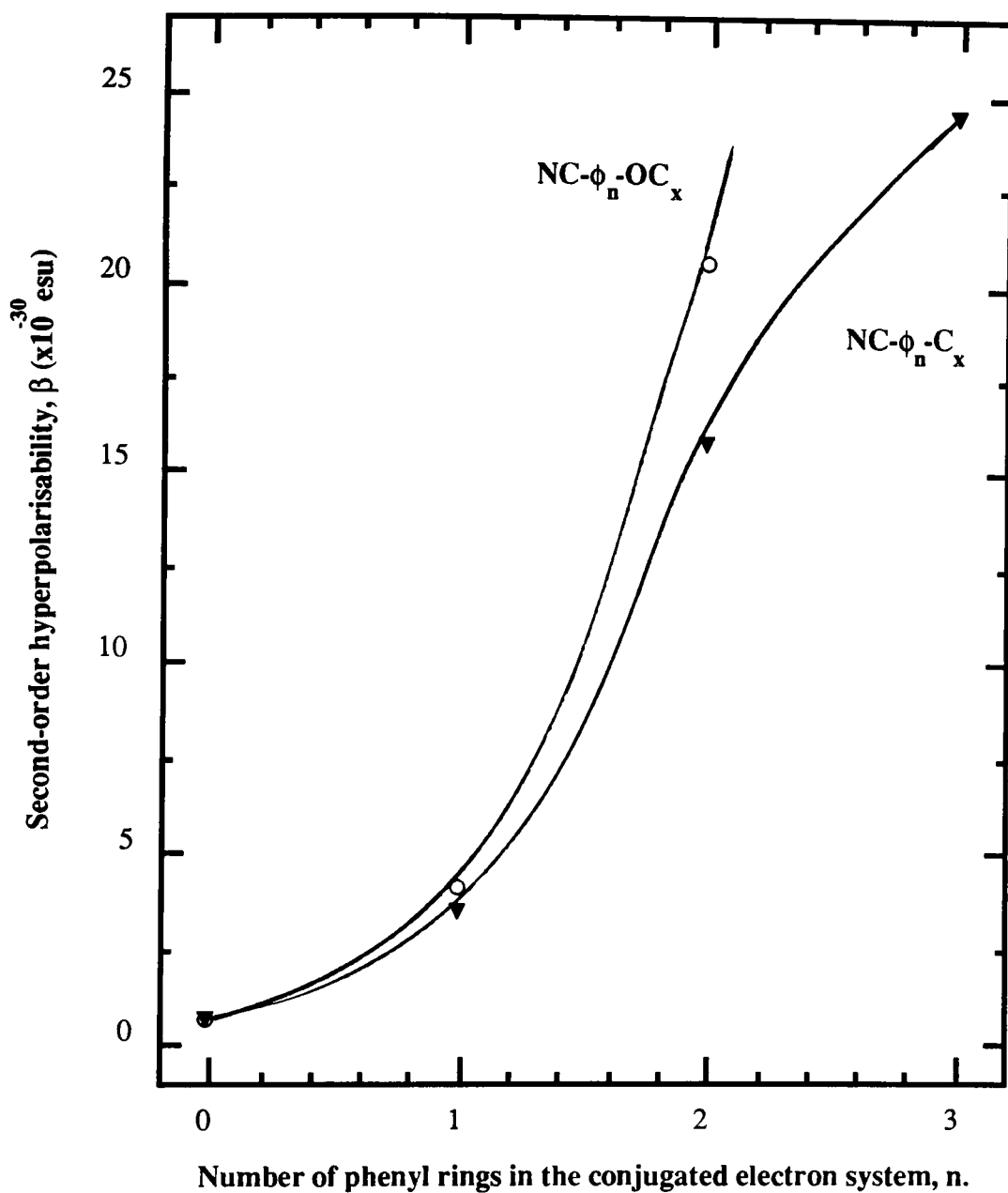


Figure 7.6 : The effect of the number of directly bonded phenyl rings on the second-order non-linear optical hyperpolarisability of molecules of the general formula $\text{NC-}\phi_n\text{-C}_x$ and $\text{NC-}\phi_n\text{-OC}_x$.

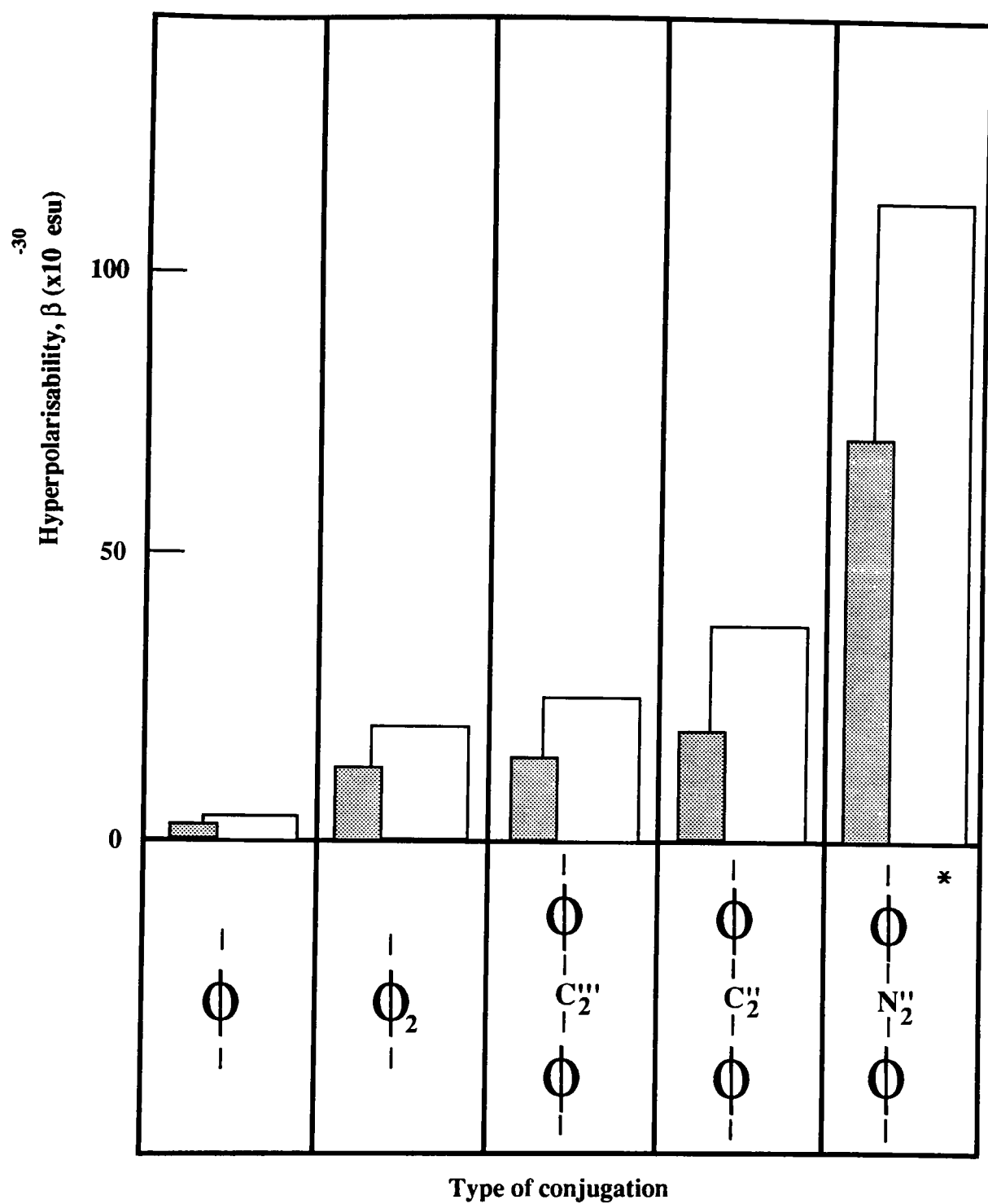
although stronger than the simple alkyl chain. Figure 7.6 shows that the β coefficient is indeed higher when the stronger OCH_3 donor is used. Only the $n=1$ and $n=2$ alkoxy compounds were available at the time of measurement although it would be expected that the coefficient of the $n=3$ molecule would increase further.

In conclusion, it is evident that β increases as the number of polarisable phenyl rings (directly bonded in this case) increases. However, it is found that the rings in the polyphenyl systems often lie out of plane with respect to each other due to steric hinderance effects. This configuration hinders the overlap of π -electron orbitals of adjacent rings thus reducing their polarisability. Such problems may often be avoided using a conjugated bridge between adjacent rings such as in the *trans*-stilbene or azobenzene compounds. These systems will be discussed in the following section.

(iii) The role of extended conjugation.

Although it has been explained above that the second-order hyperpolarisability, β , may be enhanced considerably by increasing the number of phenyl rings in the cyano(poly)phenyl precursors, a more dramatic modification to the non-linear optical properties may be achieved with other forms of extended conjugation. In this case, the aromatic rings may be coupled together via conjugated bridging links such as in the *trans*-stilbene system.

The effect of different types of conjugated electron system upon the molecular non-linearity has been studied for the general conjugated molecule $\text{NC-R}_C\text{-OC}_x$ where R_C is the conjugated electron grouping. The measured β coefficients for all the various conjugated systems investigated are presented in Figure 7.7. The off-resonance values, β_0 , will be discussed in the next section. Clearly, the hyperpolarisability increases because the number of polarisable electrons rises in the order $-\phi- < -\phi_2- < -\phi\text{-C}_2\text{''''-}\phi- < -\phi\text{-C}_2\text{''-}\phi- <$



□ Hyperpolarisability at fundamental wavelength, β .

▨ Off-resonance hyperpolarisability, β_0 .

* Measured at 1.34 μm (fundamental).

Figure 7.7 : The dependence of second-order hyperpolarisability upon the type of conjugated electron system (R_c) for the molecule $\text{NC-R}_c\text{-OC}_x$.

- ϕ -N₂"- ϕ - . A large increase in β is observed for the NC- ϕ -N₂"- ϕ -OH molecule relative to the *trans*-stilbene precursor. This occurs as the nitrogen atoms each possess a free lone pair of electrons which can be incorporated into the conjugated molecular orbital. The carbon atoms in the stilbene system have no such lone pairs which may be polarised and thus a reduced hyperpolarisability is observed. It must be mentioned that the fundamental wavelength used to measure the non-linearity of this compound was 1.34 μ m which results in a lower measured hyperpolarisability.

Clearly, the above data highlight the need for extended conjugation in the observation of a large second-order non-linear response.

(iv) Off-resonance hyperpolarisability and the efficiency-transparency trade-off.

The extension of the conjugated electron system leads to the observation of a large non-linearity as discussed above. However, it also produces another important physical effect. The increase in conjugation leads to a stabilisation of the excited states of the molecule with respect to the ground states. Thus the transition energy between the ground and first excited state is reduced and is manifested as a significant bathochromic shift in the transition wavelength. This movement of λ_{max} was discussed in detail in Chapter 5 for the precursors and the ruthenium complexes although its relevance to second-order non-linear optics was not stressed. The shift plays an important role in the non-linear response. Examination of the expression first used in Chapter 2 and shown below for clarity exposes the relationship between the magnitude of β and the transition energies:

$$\beta_{CT} = \frac{3e^2\hbar^2}{2m} \frac{W f \Delta\mu}{[W^2 - (2\hbar\omega)^2][W^2 - (\hbar\omega)^2]} \quad (7.3)$$

It is evident that the two terms on the denominator can become extremely small if the transition energy of the main absorption band is matched to the energy of either the fundamental photons (1.06 μ m) or the second-harmonic photons (0.532 μ m). Thus an enhancement of the non-linear coefficient may be produced provided the correct spectral characteristics are shown by the molecule. In the case of the nitrile precursors, the use of extended conjugation and/or strong electron donating groups causes a significant reduction in the magnitude of the term $[E^2 - (2h\nu)^2]$ in the order $-\phi- < -\phi_2- < -\phi-C_2'''-\phi- < -\phi-C_2''-\phi- < -\phi-N_2''-\phi-$. The hyperpolarisability increases in this order owing partially to the resonance enhancement effect described above. The corresponding differences in the $\lambda_{\max}$ values and the second-harmonic wavelength are 285nm, 237nm, 211nm, 188nm and 165nm respectively.

It is important, however, to be able not only to compare the non-linear response of materials at the wavelength of the exciting fundamental laser beam, as has been done already, but also to derive coefficients that neglect the resonance enhancement effect so that the frequency-independent non-linear characteristics of materials may be investigated. The ever-increasing number of available laser wavelengths with high power output that are currently being developed further highlights the need for consideration to be given to off-resonance β_0 values in order to allow meaningful comparisons of non-linear efficiencies to be made. The off-resonance β_0 value can be expressed as:

$$\beta_0 = \beta \frac{I}{\left\{ 1 - \left[\frac{l_{\max}}{l_w} \right]^2 \right\} \left\{ 1 - \left[\frac{2l_{\max}}{l_w} \right]^2 \right\}} \quad (7.4)$$

where $l_{\max}$ is the wavelength of maximum absorption of the non-linear molecule and l_w is the wavelength of the fundamental exciting laser radiation. Clearly, this expression compensates for the nearness of the molecular absorption to the fixed fundamental and

second-harmonic wavelengths. The values of β_0 for the precursors studied in this work are shown in Figures 7.4 and 7.7. The difference in the value of β and β_0 becomes significantly larger in the series $-\phi- < -\phi_2- < -\phi-C_2'''-\phi- < -\phi-C_2''-\phi- < -\phi-N_2''-\phi-$ indicating that the shift in transition energy, brought about by increasing the conjugation, makes an increasingly dramatic contribution to the total absolute hyperpolarisability as the energy of the absorptive transition approaches the second-harmonic photon energy [115].

Two important considerations must therefore be given to the resonance effect. Firstly, β_0 values should be used where molecular efficiencies need to be compared realistically with respect to each other. Secondly, if a fixed fundamental exciting laser wavelength is chosen for a particular device application, the molecular absorption must be engineered to allow the resonance condition to be approached although *not too closely* otherwise the generated second-harmonic radiation is self-absorbed by the medium itself. This efficiency-transparency trade-off emphasises the important role of the organic synthetic chemist in the molecular design of new materials for non-linear optics, and the need for interdisciplinary collaboration between chemists, physicists and device specialists if the goal of an organic-based non-linear integrated optics device is to be realised.

7.2.4 Summary.

The data presented and analysed in section 7.2 have enabled the relationship between the magnitude of the non-linear optical response of the precursor compounds and their intricate molecular structure to be understood. The importance of electron donation, conjugated electron systems and the resonance enhancement effect has been stressed. The investigation has allowed estimates of the second-order hyperpolarisabilities of the ruthenium complexes to be made; these will be discussed in the following section. Clearly, further breakthroughs in the field of non-linear optical materials design depends upon the co-operation of researchers from many scientific and technical backgrounds.

7.3 Non-linear optical properties of the ruthenium complexes.

7.3.1 Introduction.

The non-linear optics data regarding the nitrile precursor molecules described in the previous chapter were collected in order to study the relationship between the magnitude of the non-linear response and the molecular structure. However, a knowledge of the spectral characteristics of the ruthenium complexes and the second-order non-linear coefficients of the precursors has enabled the hyperpolarisabilities of the complexes themselves to be estimated.

The powders [116] of all the ruthenium complexes studied gave no second-harmonic generation (SHG) when placed in the path of a Nd:YAG laser beam. The molecular hyperpolarisabilities are expected to be relatively large ($> 20 \times 10^{-30}$ esu) so it can be assumed that the crystal structures must be centrosymmetric and therefore no advantage is taken of the inherent molecular non-linearity to yield a macroscopic response.

The LB deposition process is an attractive method with which the individual molecules may be aligned in an ordered array in order to allow the molecular non-linearities to be exposed in the bulk structure. In a single monolayer the molecules are packed in a two-dimensional non-centrosymmetric crystal lattice. The degree of control in thickness and structural architecture afforded by the technique enable organic compounds to play an important role in non-linear physical applications. There have been many problems with the measurement of SHG from LB films of the organo-ruthenium complexes, although the information obtained has exposed areas of molecular design to which greater attention should be given in future research on this class of materials.

Some work has also been carried out to examine the non-linear response of mixed layers including the Ru- ϕ_3 -C₅ x : NC- ϕ_3 -C₅ y system discussed in Chapters 5 and 6. The results are summarised and discussed realistically in the context of their potential use for non-linear optical devices.

7.3.2 Estimation of the second-order non-linear optical hyperpolarisabilities of the organo-ruthenium molecular complexes.

The main purpose of studying the second-order non-linearity of the precursor molecules was to enable the expected response of the ruthenium complexes to be predicted. In this sub-section, it will be shown how such estimates may be made using spectral information described in Chapter 5. The substitution of the ruthenium group onto the cyano group of the precursor induces further withdrawal of electron density from the conjugated system thus red-shifting the position of $\lambda_{\max}$. Therefore, the hyperpolarisability is affected by this change. Equation 7.1 relates the hyperpolarisability to the spectral properties of the non-linear material as discussed in section 7.2 :

$$\beta = \left(\frac{3e^2 h^2}{8\pi^2 m} \right) \frac{W f \Delta\mu}{[W^2 - E_{\omega}^2][W^2 - E_{2\omega}^2]} \quad (7.5)$$

In this equation the term $(3e^2 h^2 / 8\pi^2 m)$ is a constant which will be referred to as k, W is the energy difference corresponding to the absorptive transition from ground to first excited state, f is the oscillator strength of the transition, $\Delta\mu$ is the change in dipole moment from the ground to the excited state and $E_{\omega, 2\omega}$ is the energy of the fundamental and second-harmonic photons respectively. The relations below may therefore be written for β_{Ru} (the hyperpolarisability of the ruthenium complex) and β_p (that of the precursor):

$$\beta_{Ru} = k \frac{W_{Ru} f_{Ru} \Delta\mu_{Ru}}{[W_{Ru}^2 - E_{\omega}^2][W_{Ru}^2 - E_{2\omega}^2]} \quad (7.6)$$

$$\beta_p = k \frac{W_p f_p \Delta\mu_p}{[W_p^2 - E_\omega^2][W_p^2 - E_{2\omega}^2]} \quad (7.7)$$

The oscillator strength, to a first approximation, can be considered to be directly proportional to the molar absorption coefficient, $\epsilon_{\max}$, at the wavelength of maximum absorption (Chapter 5). Also, because the complexation of the ruthenium headgroup to the nitrile precursor does not affect significantly the length of the conjugation of the molecule, the value of $\Delta\mu_{Ru}$ is assumed to be equal to $\Delta\mu_p$. The expression for the ratio β_{Ru}/β_p can therefore be simplified to:

$$\frac{\beta_{Ru}}{\beta_p} = \frac{W_{Ru} \epsilon_{Ru}^{\max}}{W_p \epsilon_p^{\max}} \frac{[W_p^2 - E_\omega^2][W_p^2 - E_{2\omega}^2]}{[W_{Ru}^2 - E_\omega^2][W_{Ru}^2 - E_{2\omega}^2]} \quad (7.8)$$

β_{Ru}/β_p is therefore the factor by which β_p must be multiplied to yield the value for the ruthenium complex. Table 7.2 shows the estimated β values of the six most efficient complexes. Clearly, the complexes Ru- ϕ -N₂"- ϕ -NMe₂ and Ru- ϕ -N₂"- ϕ -NMeC₇ possess far larger coefficients than any of the other complexes. This is a direct result of the strongly electron donating -NMe₂ and -NMeC₇ groups coupled to the highly polarisable electron density of the azobenzene conjugated electron system. In addition to the close approach of $\lambda_{\max Ru}$ to the resonance condition, it can be seen that the value of $\epsilon_{\max}$ is nearly doubled for both complexes such that $\epsilon_{\max Ru}/\epsilon_{\max p}$ is large. On the contrary, virtually no change in $\epsilon_{\max}$ is observed for complex Ru- ϕ -OC₁₂ and its corresponding precursor and this is reflected in its β_{Ru} value.

Table 7.3 shows the values of the β coefficients for several compounds studied in other research groups. It can be seen that complex Ru- ϕ -N₂"- ϕ -NMeC₇ compares favourably with the hemicyanine [117] and DPNA [118] molecules which were studied in

Complex	β_p $\times 10^{-30}$ esu	$\lambda_p^{\max}$ nm	$\lambda_{Ru}^{\max}$ nm	$\epsilon_p^{\max}$ $\text{mol}^{-1} \text{cm}^{-1}$	$\epsilon_{Ru}^{\max}$ $\text{mol}^{-1} \text{cm}^{-1}$	$\frac{W_{Ru} \epsilon_{Ru}^{\max}}{W_p \epsilon_p^{\max}}$	$\frac{(W_p^2 - E_\omega^2)(W_p^2 - E_{2\omega}^2)}{(W_{Ru}^2 - E_\omega^2)(W_{Ru}^2 - E_{2\omega}^2)}$	β_{Ru} $\times 10^{-30}$ esu
$\text{Ru-}\phi_3\text{-C}_5$	23.8	303	307	39.0	61.7	1.5616	1.0694	40
$\text{Ru-}\phi_2\text{-OC}_{12}$	20.0	295	332	28.8	29.0	0.8948	1.8601	33
$\text{Ru-}\phi\text{-C}_2'''\text{-}\phi\text{-OC}_{14}$	25.4	321	355	22.1	30.2	1.2357	1.7521	55
$\text{Ru-}\phi\text{-C}_2''\text{-}\phi\text{-OC}_{13}$	37.0	344	368	29.5	31.4	0.9951	1.4850	59
$\text{Ru-}\phi\text{-N}_2''\text{-}\phi\text{-OH}$	113.0*	367	382	22.1	23.2	1.0086	1.2251	140
$\text{Ru-}\phi\text{-N}_2''\text{-}\phi\text{-NMe}_2$	139.0*	451	486	17.7	35.7	1.8713	1.5910	414
$\text{Ru-}\phi\text{-N}_2''\text{-}\phi\text{-NMeC}_7$	160.0**	462	498	24.7	41.8	1.5699	1.6152	406

* Measured using a fundamental wavelength of 1.34 μm .

** Estimated by considering the enhancement effect of the -NMeC₇ group relative to the -NMe₂ group.

Table 7.2 : Estimated second-order non-linear optical hyperpolarisabilities of several ruthenium complexes showing the dramatic increase in value for the azobenzene conjugation coupled to the strongly donating amine-type group.

Compound	Hyperpolarisability, β $\times 10^{-30}$ esu
$(C_{16})_2-N-\phi-C_2''-\phi^{N+}-C_1$	2000
$Ru-\phi-N_2''-\phi-NMeC_7$	405
Hemicyanine	310
DPNA	310

Table 7.3 : A comparison of the hyperpolarisabilities of some of the most efficient LB molecules for second-order non-linear optics.

1987 although the compound $(C_{16})_2N-C_2''-\phi^{N+}-C_1$ [119] exhibits a huge value due to the powerful pyridinium ion electron acceptor (the symbol ϕ^{N+} indicates a heterocyclic nitrogen which replaces a carbon atom of the phenyl ring in the *para* position). It should be mentioned that a ruthenium complex $(C_x)_2N-\phi-N_2''-\phi^{N+}-Ru$ is currently being synthesised and is expected to possess a similarly large hyperpolarisability.

7.3.3 Non-linear optical behaviour of organo-ruthenium LB films.

The following sections are concerned with the second-order non-linear properties of LB films of the organo-ruthenium complexes. Particular attention has been given to complex $Ru-\phi_3-C_5$ as an example of the compounds studied. By far the greatest obstacle to the measurement of the non-linear coefficients of the molecules in LB film form has been found to be laser damage. Nevertheless, the lessons learnt from experiencing these difficulties should reduce the task of future workers in selecting potentially useful materials.

Unfortunately, time has not permitted a thorough non-linear optics investigation to be made on the most promising and exciting complex yet studied. Work is currently in progress to assess the nonlinearity of the complexes $Ru-\phi-N_2''-\phi-OC_{16}$ and $Ru-\phi-N_2''-\phi-NMeC_7$. Some investigations on mixed layer systems have also been made and the relevant results are discussed.

(i) Non-linear response of $Ru-\phi_3-C_5$ LB layers.

Although in section 7.3.2 the β coefficients are shown to be relatively high for some of the more recently synthesised ruthenium complexes, two features must be borne in mind. Firstly, the ruthenium (η^5 -cyclopentadienyl)-(bis triphenylphosphine) hexafluorophosphate head group is large ($1.3nm^2$) compared to many other LB materials

(0.2 - 0.5nm²). This means that the corresponding macroscopic susceptibility, $\chi^{(2)}$, is relatively small and that the detection of the second-harmonic generation from the ruthenium complexes may be very difficult. Indeed this has proved to be the case. It must be emphasised, however, that this particular head group was chosen to enable the physical properties of all the compounds to be mutually compared with the eventual intention of reducing its area by substitution of physically smaller ligands in order to increase the molecular packing density and the resulting $\chi^{(2)}$ value. This work will be discussed in the next chapter.

The data below are for the complex Ru- ϕ_3 -C₅ which was not susceptible to laser damage. Figure 7.8 shows the second-harmonic (0.532 μ m) generation from a single crystal quartz plate which was used as the standard reference material for SHG studies on organic films. The experimental procedure has been outlined in Chapter 4 and will not be revised here. The variation in the output intensity from the quartz as it is rotated about its vertical axis (which is normal to the fundamental propagation direction) takes the form of a well-defined Maker fringe pattern. Such a pattern originates from the phase mismatch that occurs because of the dispersion properties of the refractive index of quartz. The fundamental beam at ω experiences a refractive index of n_ω whilst the generated second-harmonic beam observes an index of $n_{2\omega}$. Thus the waves travel at slightly different velocities and therefore the second-harmonic waves generated at different points in the quartz periodically become in and out of phase with each other. The use of quartz as a reference simply ensures that the photomultiplier used in the experimental set-up is calibrated.

In contrast, the fringe pattern obtained from a monolayer of the Ru- ϕ_3 -C₅ complex (coated on both sides of the substrate), shown in Figure 7.9, exposes a different angular dependence. Indeed, this pattern has no connection whatsoever with Maker fringes. It originates from the natural dispersion of the substrate ($n_{2\omega}^\sigma - n_\omega^\sigma$) which introduces a

Figure 7.8 : The Maker fringe pattern obtained from a single crystal quartz plate when it is rotated about its vertical axis (which is normal to laser beam direction).

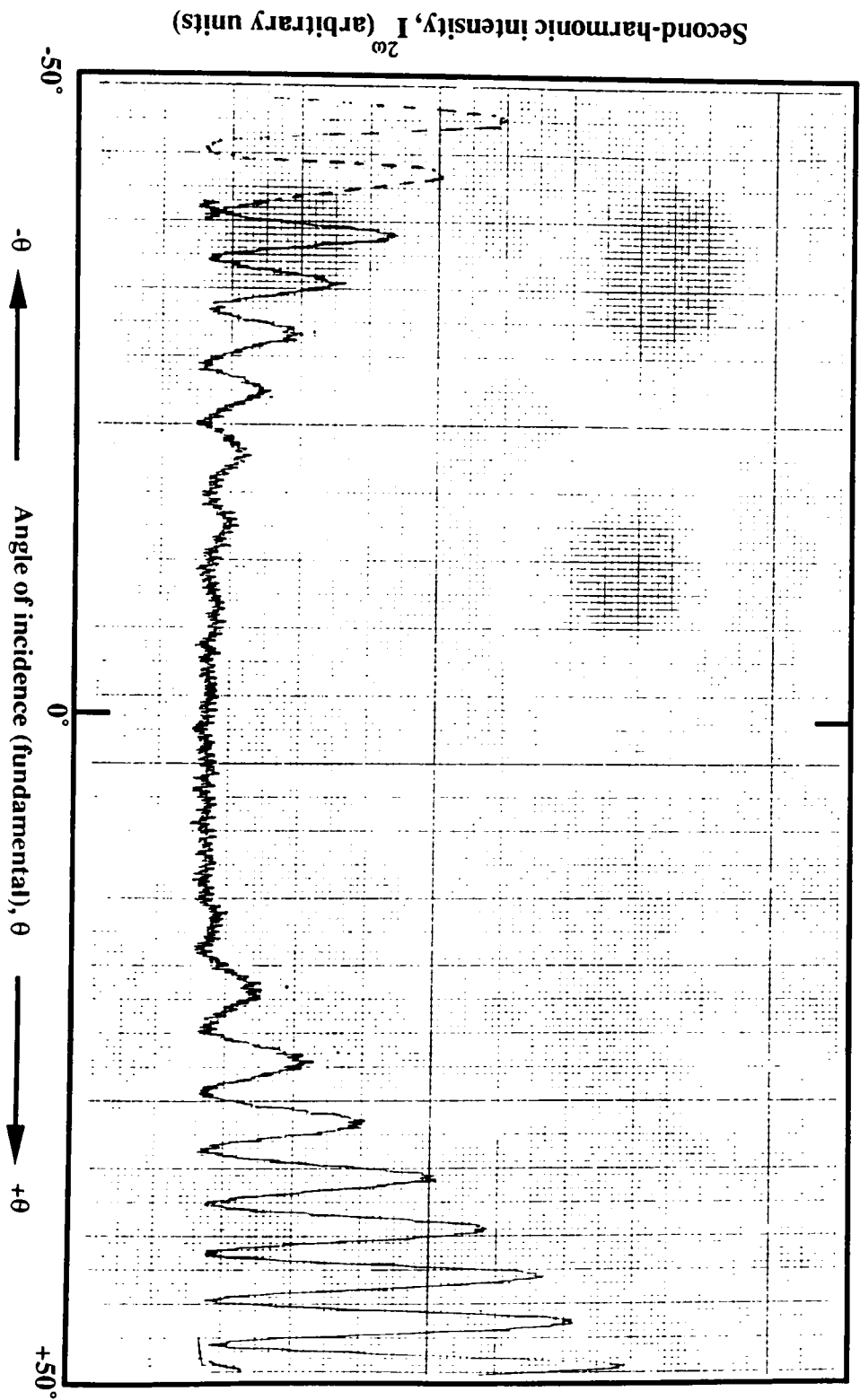


Figure 7.9 : The second-harmonic interference fringes from a monolayer of complex Ru- ϕ_3 coated on both sides of a Corning 7059 glass substrate

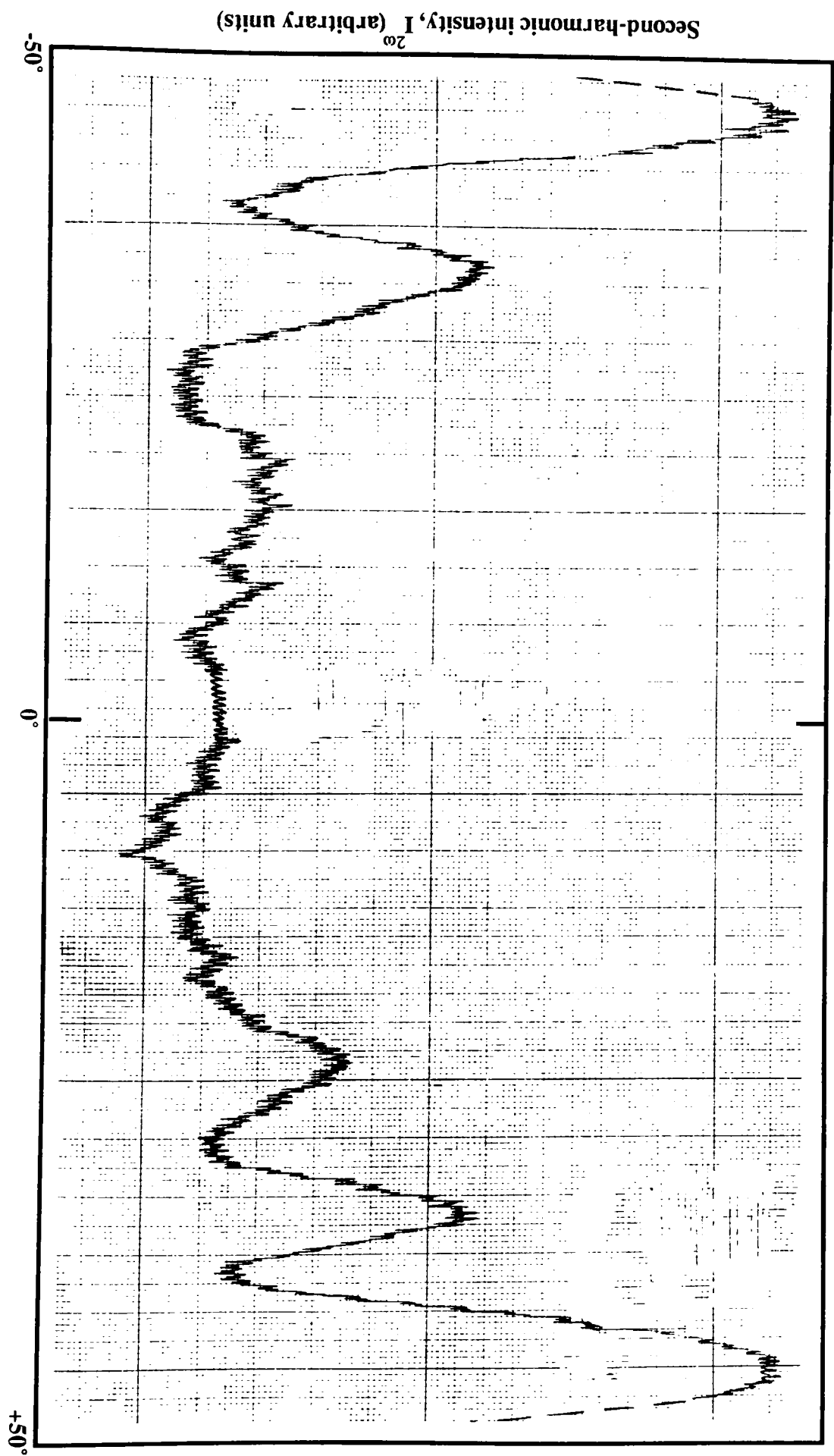
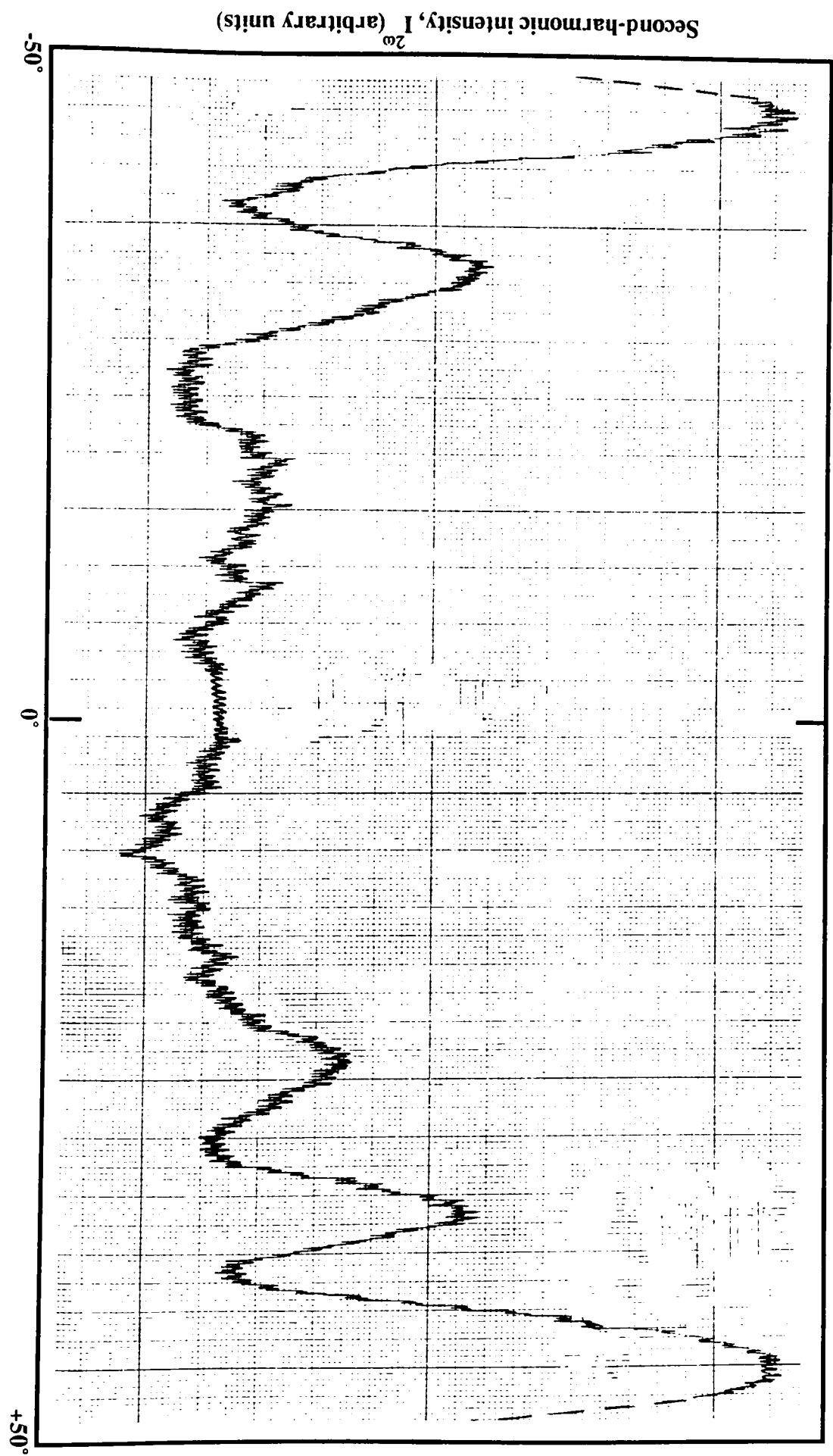


Figure 7.9 : The second-harmonic interference fringes from a monolayer of complex Ru- ϕ_3 coated on both sides of a Corning 7059 glass substrate



dephasing factor between the harmonic waves generated at the front and back sides of the substrate. Here $n_{2\omega}^{\sigma}$ and n_{ω}^{σ} are the refractive indices of the second-harmonic and fundamental waves in the substrate respectively. $\chi^{(2)}$ values are determined by comparison of the amplitude of the envelope of the LB fringes with the signal from the quartz reference plate. The measured hyperpolarisability of the complex Ru- ϕ_3 -C₅ was found to be $46 \pm 5.0 \times 10^{-30}$ esu. This value is in good agreement with that predicted using the EFISHG precursor data.

It was mentioned in Chapter 4 that the relationship between second-harmonic intensity emitted from a multilayer LB film is expected to obey a square law dependence with thickness since the phase mismatch within the LB film itself is negligible and may be ignored. Figure 7.10 shows the variation in the emitted light intensity at the second-harmonic wavelength as a function of the square of the number of transferred monolayers. The relation is linear suggesting that the order and alignment of non-linear molecules within individual monolayers is maintained throughout the multilayer structure.

The above results have shown that SHG can be observed from the Ru- ϕ_3 -C₅ complex. However, the size of the head group effectively reduces the $\chi^{(2)}$ value so that a *large* macroscopic response is not observed. The proposed packing of the ruthenium head groups (refer to Chapter 5) leads to large voids between the terphenyl chains of adjacent molecules which may, as has been shown in the precursor incorporation studies, be filled with molecules of the corresponding precursor compound. The resultant effect upon the second-order non-linearity of incorporating the precursor molecules has been found to increase by approximately 50%. Figure 7.11 displays the intensity profile of the second-harmonic beam emitted from a monolayer of (a) Ru- ϕ_3 -C₅ and (b) a mixed monolayer of Ru- ϕ_3 -C₅³⁵: NC- ϕ_3 -C₅⁶⁵. The increase in signal strength reflects the increase in the number of aligned active non-linear molecules in the monolayer and the probable improvement in the film structure.

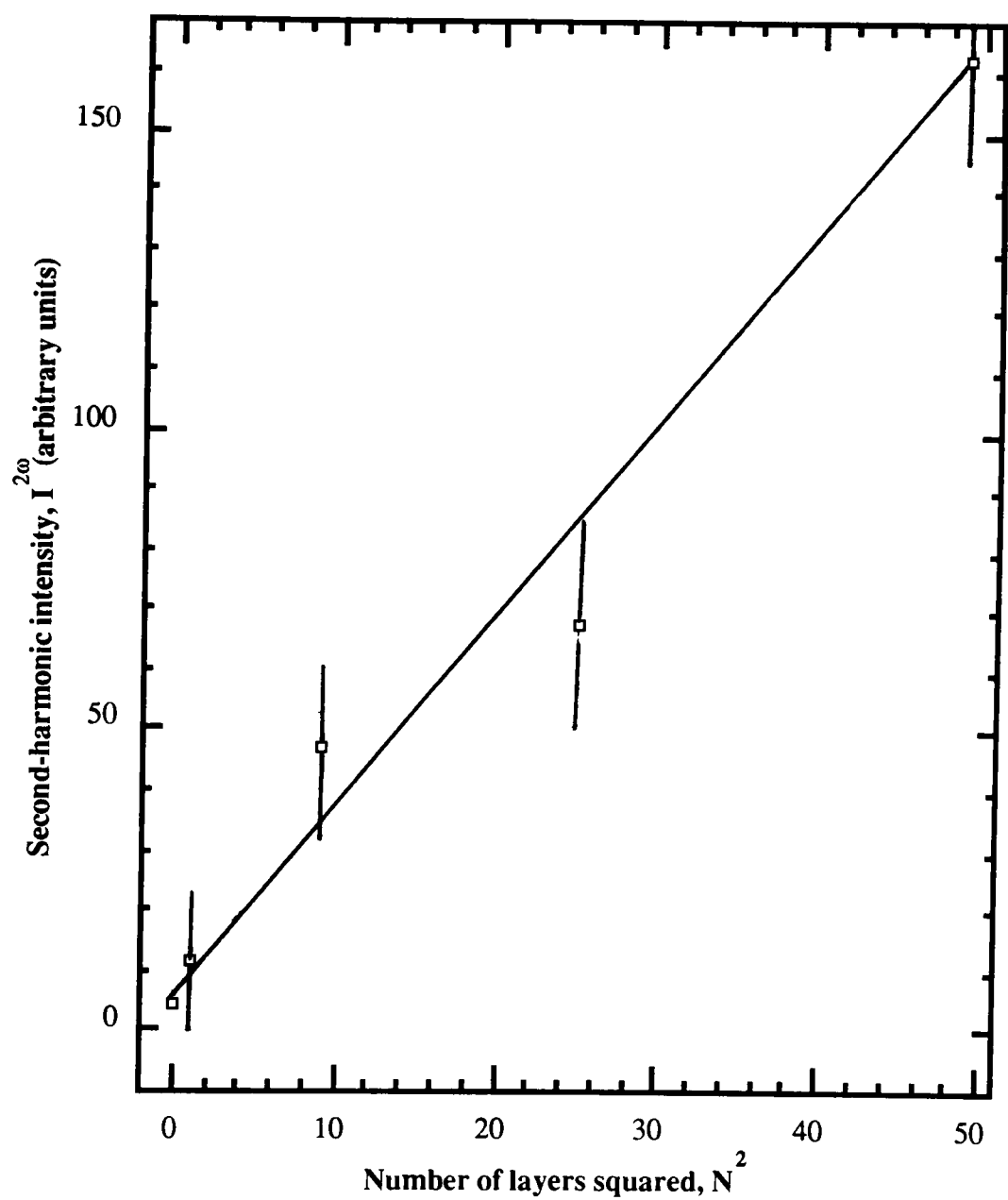


Figure 7.10 : The thickness dependence of the second-harmonic light intensity emitted from LB films of complex $\text{Ru-}\phi_3\text{-C}_5$ deposited onto both sides of a Corning 7059 glass substrate.

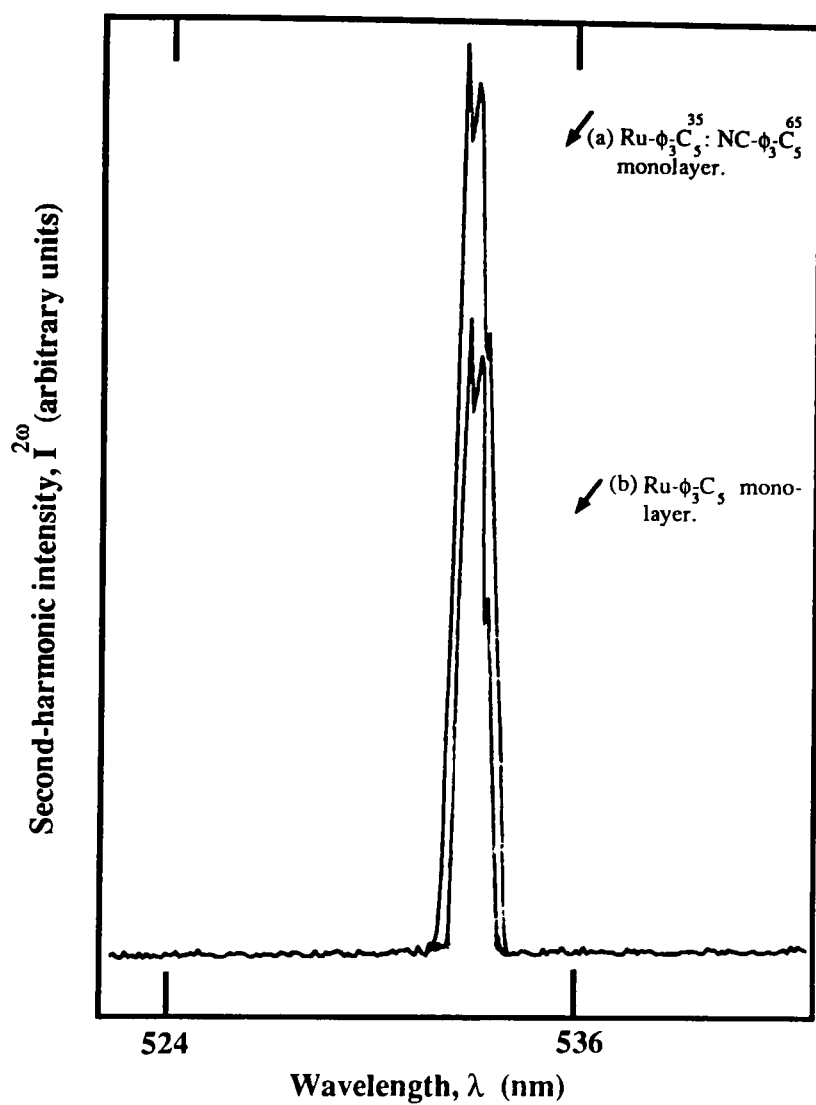


Figure 7.11 : Enhancement of the second-harmonic response of a $\text{Ru-}\phi_3\text{C}_5$ monolayer by incorporation of precursor molecules in the ruthenium lattice.

The above data have shown that SHG can be obtained from the terphenyl ruthenium complex and that its dipole density may be increased to yield an enhanced non-linear response. It is believed that with a smaller headgroup and a reduction in the scattering losses [120], the macroscopic response will be sufficiently large to allow incorporation into optical devices. The modification of the surface plasmon resonance equipment to enable electro-optic coefficients to be determined will provide a much more convenient means of testing the second-order non-linear optical efficiency of the ruthenium complex LB films. The bulk powder melting point of this complex is 131°C. Many of the complexes whose LB structures are likely to deteriorate below about 100°C were found to suffer adverse laser damage. Their behaviour is described in the next section.

(ii) Laser damage aspects.

It was found that the LB films of several of the ruthenium complexes suffered intolerably from the heating effect of the YAG laser beam. Although the pulse period was typically only 10ns, the scattering and absorption within the film caused damage especially to those compounds whose bulk melting points were relatively low. The heat generated was often extreme enough to cause burning of material which could be detected by a sudden spike response of the photomultiplier. Figure 7.12 indicates this vividly for complex Ru- ϕ -OC₁₇ (whose LB film breakdown temperature is 80°C). As soon as damage has occurred, the remaining non-linear response will be dramatically different owing to loss of material and severe molecular rearrangement and a meaningful measurement of the hyperpolarisability is not possible. The constructive lesson to be gained from such phenomena as these is that the thermal and mechanical stability should be improved as much as possible and that care should be taken to minimise the number of scattering centres within the LB structure.

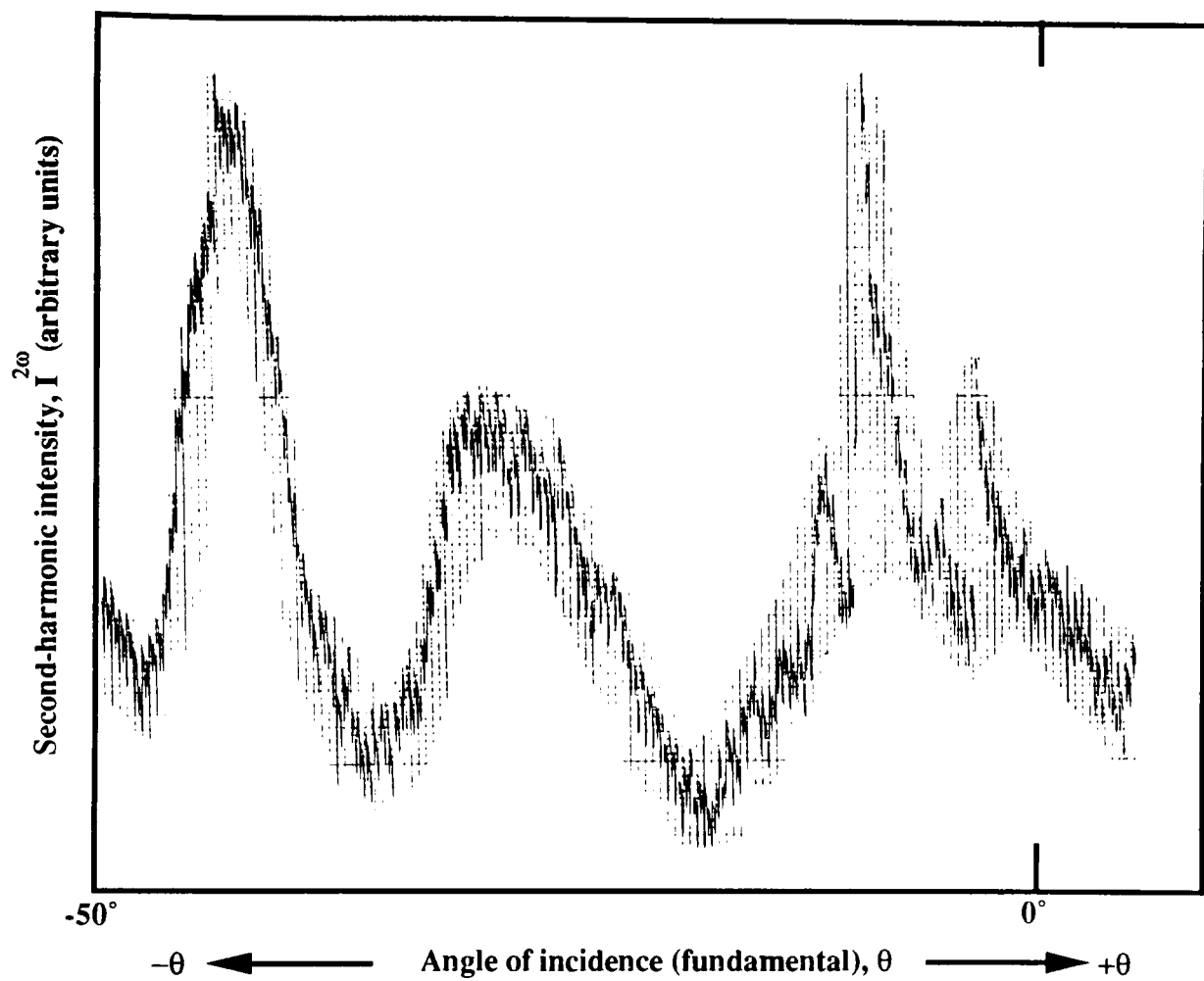


Figure 7.12 : Burning of material in the LB film of complex $\text{Ru-}\phi\text{-OC}_{17}$ caused by the heating effect of the YAG laser beam.

7.4 Pyroelectric properties of organo-ruthenium complexes.

7.4.1 Introduction.

This section is concerned with the study of the pyroelectric characteristics of the ruthenium complexes. Their static pyroelectric behaviour will be discussed and possible mechanisms that give rise to the phenomenon will be considered. The pyroelectric coefficients may be dramatically increased using heterogeneous layers although the resulting thermal stability of the LB structures is degraded. It is envisaged that the use of behenic acid in the mixed layers improves the structure of the films and the degree of alignment within each monolayer.

It should be noted that the research into the pyroelectric properties of these materials was initiated upon the realisation that the molecules developed throughout the course of this work possessed large ground state dipole moments which may be temperature dependent. The knowledge that they could be ordered and preferentially aligned within a non-centrosymmetric solid LB film suggested that the complexes could be of great potential use in the field of pyroelectric imaging. Indeed, their interest has merited a further concurrent doctoral project. The author is thus indebted to Mr. R. Colbrook who performed the experiments on the complexes which will be described below.

7.4.2 Static pyroelectricity in homogeneous organo-ruthenium LB films.

In Chapter 3, the phenomenon of pyroelectricity was introduced and it was emphasised that in order for a pyroelectric current to flow (section 3.3) the macroscopic structure of the active material must be non-centrosymmetric and that the total polarisation must change with temperature. On a molecular level, this condition implies that the magnitude of the measured component of the dipole moment must be temperature

dependent and that each molecular change must be augmented by similar behaviour on neighbouring molecular sites throughout the structure. This constructive development of a change in the macroscopic polarisation can only occur in a non-centrosymmetric medium. For this reason, alternate layer superlattices of the ruthenium complexes have been studied. The pyroelectric current i_p can be expressed as:

$$i_p = p A \frac{dT}{dt} \quad (7.9)$$

where i_p is the pyroelectric current (that flows in the circuit shown in Figure 3.11 in Chapter 3) which therefore depends upon the magnitude of the static pyroelectric coefficient, p , and the rate of change temperature of the medium. Table 7.4 shows the static coefficients (measured at 15°C using a typical temperature ramp rate of 0.1K per minute) for six of the complexes when the ruthenium monolayers within the superlattice are themselves homogeneous. It is evident that in the sub-group Ru- ϕ_n -C_x the coefficient increases as n decreases. Also the response can be improved when an alkoxy donor is used as in complexes Ru- ϕ -OC₁₂ and Ru- ϕ -OC₁₇.

Two possible mechanisms for the change in polarisation within these materials have been suggested. Firstly, a reordering process in which the ruthenium molecules tilt would lead to a change in the component of polarisation normal to the substrate plane. In liquid crystal molecules, such tilting behaviour is often observed [121]. Secondly, the ionic nature of the complexes means that a large dipole moment exists near the head group unlike that which results from the redistribution of electron density associated with the conjugated phenyl ring systems. It is possible that the relative separation of the ions could be temperature dependent which would lead to the observation of pyroelectricity. Much work is currently in progress to elucidate the exact nature of the process(es) from which

Ruthenium Complex	Pyroelectric Coefficient $p \text{ (}\mu\text{C m}^{-2} \text{ K}^{-1}\text{)}$
$\text{Ru-}\phi\text{-C}_3\text{C}_5$	-0.01
$\text{Ru-}\phi\text{-OC}_2\text{C}_{12}$	-0.04
$\text{Ru-}\phi\text{-C}_{12}$	-0.25
$\text{Ru-}\phi\text{-OC}_{17}$	-0.45
$\text{Ru-}\phi\text{-OC}_{12}$	-0.50

Table 7.4 : The static pyroelectric coefficients of several of the organo-ruthenium complexes showing the dependence upon molecular structure.

the pyroelectric response originates and therefore no claim to their detailed understanding is made here.

7.4.3 Heterogeneous ruthenium LB films for pyroelectricity.

The pyroelectric coefficient of a material is directly proportional to the change in polarisation that results in response to a unit change in temperature per unit volume. Thus, if the ordering and alignment of the ruthenium molecules within a monolayer were *independent* of the composition within a two-component mixed film, it would be expected that the highest coefficients would be observed for the films containing very high molar fractions of the complex. In order to investigate the relationship between the pyroelectric response and the mixed layer composition, various molar ratios of the Ru- ϕ -OC₁₇^x : behenic acid^y system were studied. Figure 7.13 shows the result that an enormous increase in the coefficient is obtained for the Ru- ϕ -OC₁₇⁷⁰ : behenic acid³⁰ mixture. This relationship occurs as a result of a trade-off between the maximisation of the number of active ruthenium molecules per unit volume and the modification to the structural quality of the multilayer film. Clearly, at the 0.7 : 0.3 composition, the optimum conditions are satisfied to allow the greatest change in polarisation to occur per Kelvin change in temperature.

7.4.4 Device considerations.

The pyroelectric coefficients measured for the ruthenium complexes discussed above are some of the largest values reported for LB film materials. However, their activity relative to polymeric and single crystal materials such as PVdF and triglycine sulphate is low. The figure of merit which determines the practical use of a compound has been shown to be p/ϵ_r [122] where ϵ_r is the relative permittivity and it is because of this that the ruthenium LB films are currently attracting a great deal of attention.

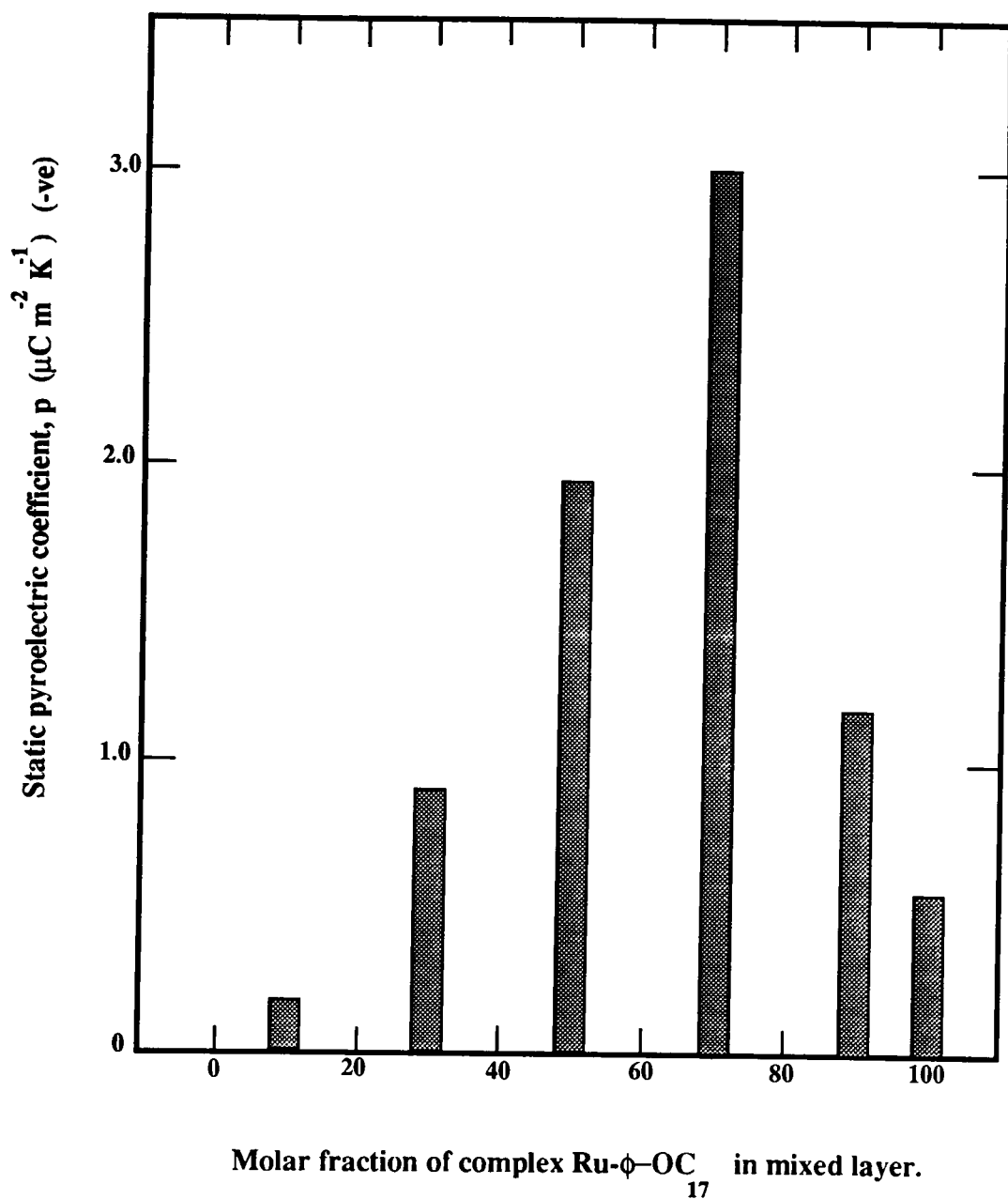


Figure 7.13 : The static pyroelectric coefficients of multilayer LB film samples of the mixed system $\text{Ru-}\phi\text{-OC}_{17}^{\text{r}}$: behenic acid^r showing the trade-off between the maximisation of the polarisation change per unit volume and the structural quality.

Material	Pyroelectric Coefficient $p \text{ (}\mu\text{C m}^{-2} \text{ K}^{-1}\text{)}$	Relative Permittivity ϵ_r	$\frac{p}{\epsilon_r}$ $p \text{ (}\mu\text{C m}^{-2} \text{ K}^{-1}\text{)}$
PLZT (ceramic)	1700	3800	0.45
PVdF (Polymer)	30	12	2.5
Liquid crystal	2.5	12	0.2
Ru-ϕ-OC₁₇ (LB Film)	3.0	4	0.75

Table 7.5 : A comparison of materials useful for pyroelectricity showing their relative figures of merit.

At frequencies in the range 0 -10kHz and in the temperature domain 25 - 65°C, the values of ϵ_r are typically very small (<10) compared to high values shown by polymers, single crystals and ceramics (12 - 3800). Table 7.5 indicates the relative activity of the complexes compared to other alternative media and shows that, even though their detailed investigation is still in its youth, the values compete favourably.

7.4.5 Future prospects.

The future for ruthenium complexes in pyroelectric technology appears to be very promising although much work remains to be done. This includes a detailed analysis of their dielectric properties, further improvement in their thermal stability, maximisation of the pyroelectric response itself and the optimisation of a plethora of supporting device parameters in order to ensure that full advantage is taken of the inherent molecular attributes exhibited by these materials.

CHAPTER 8

Conclusions and Future Research Proposals.

The work undertaken in this research project has led to the development of a novel class of thermally stable organo-metallic compounds which have allowed the relationships between the molecular structure, the LB film-forming properties and the non-linear physical characteristics to be investigated.

The complexation of the ruthenium headgroup to the precursors has shown that many nitrile compounds can now be modified to enable LB deposition to occur which would otherwise not have been possible. The organo-ruthenium complexes have been characterised in detail using many experimental techniques. Their spectroscopic properties in solution, Langmuir film and LB film form have been related to the intricate molecular structure. The resulting wavelength shifts (from the solution transitions) have yielded interesting data regarding the change in orientation and environment that the molecules experience in the Langmuir and LB phases. The complexes can be transferred onto solid substrates with a high degree of control over film thickness and molecular architecture. Several techniques, including the quartz microgravimetric method, SPR and ellipsometry, have confirmed that the deposition is uniform and reproducible.

It is possible to produce non-centrosymmetric multilayer films which exhibit second-order non-linear physical effects such as OSHG and pyroelectricity. The non-linear optical hyperpolarisabilities of both the precursors (using EFISHG) and the ruthenium complexes have been estimated and related to the electronic conjugation and the influence of electron donor and acceptor functionalities. The highest molecular coefficients for the complexes are approximately 400×10^{-30} esu for $\text{Ru}-\phi-\text{N}_2''-\phi-\text{NMe}_2$ and $\text{Ru}-\phi-\text{N}_2''-\phi-\text{NMeC}_7$ which are considerably larger than the well-known hemicyanine and nitrostilbene derivatives.

The study of the non-linear optical properties of the ruthenium LB films has provided a launching pad for future research; many of the difficulties experienced such as laser damage due to scattering [123] can be overcome by improvements to the structural order and thermal stability of the films. The resulting materials will possess large macroscopic susceptibilities and satisfy the stability requirements to render them commercially attractive for optical device applications. Figure 8.1 indicates how the bulkiness of the present ruthenium headgroup may be reduced by the replacement of the triphenylphosphine ligands with much smaller *trimethylphosphine* groups. Molecular modelling has predicted that the cross-sectional area would be $0.5 - 0.6 \text{ nm}^2$ which would lead to a 2 - 3 fold increase in surface molecular packing density within the deposited LB film. Therefore, the macroscopic $\chi^{(2)}$ coefficient would similarly increase. Preliminary studies have shown that such a molecule forms stable Langmuir films with a much reduced molecular area.

The incorporation of a heterocyclic nitrogen atom within the phenyl ring nearest to the ruthenium group will greatly improve the electron withdrawing properties of that end of the molecule. The pyridine-type complexes shown in Figure 8.1 will be synthesised shortly and should yield a much improved non-linear optical response. It has been estimated that the hyperpolarisability will be approximately 770×10^{-30} esu.

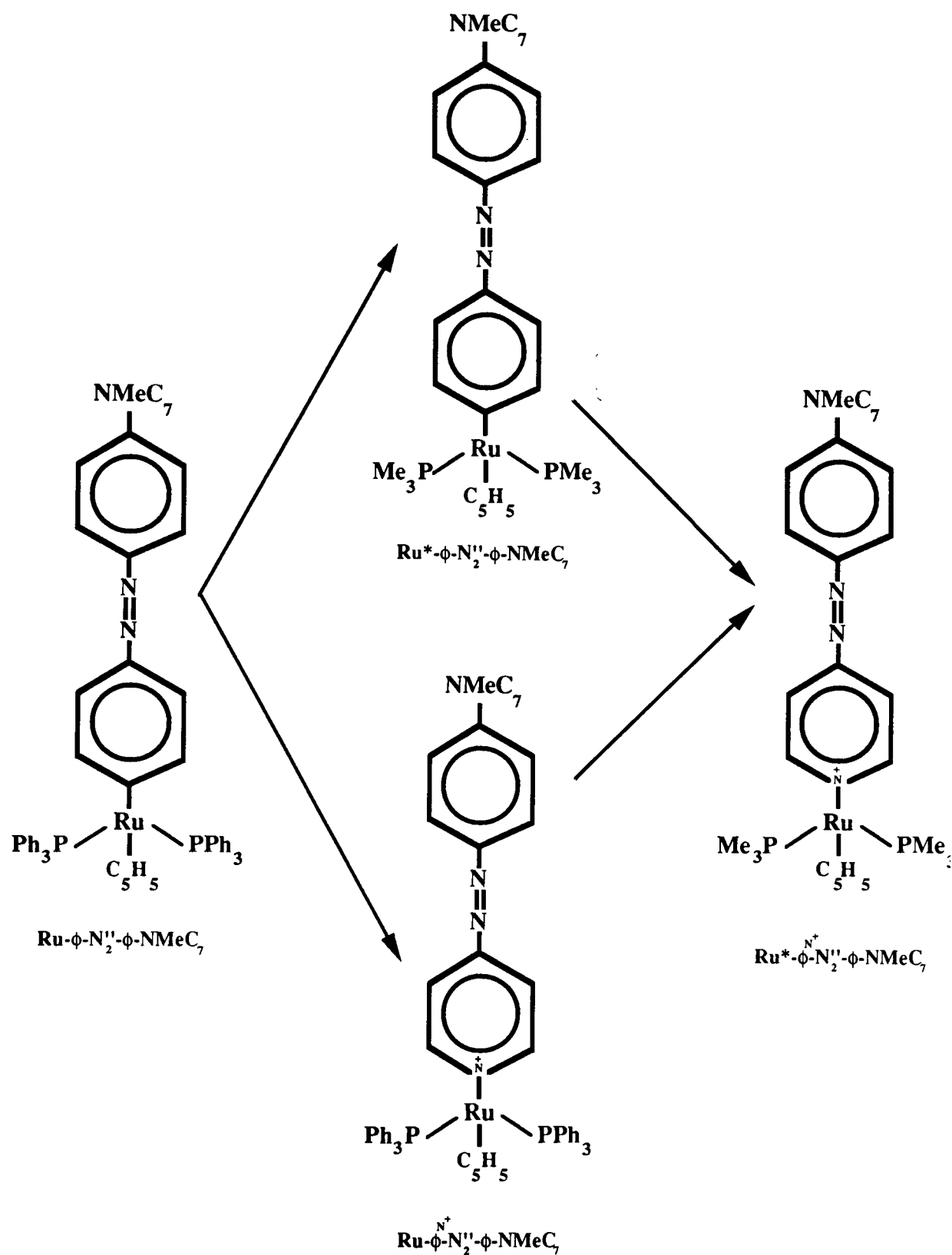


Figure 8.1 : The proposed new design features of the organo-ruthenium complex for non-linear optics.

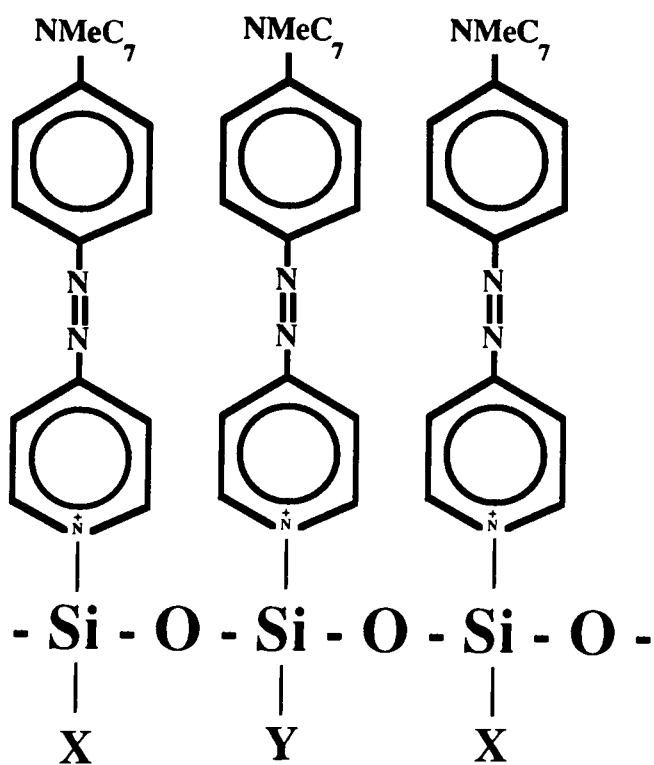


Figure 8.2 : The polysiloxane system in which the non-linear optical molecules are attached as "pendant" side-chains onto the siloxane backbone. Groups X and Y could be hydrophilic acid groups and need not be identical.

Attention must also be focused upon improving the structure of the ruthenium LB films whilst maintaining high thermal stability and non-linear optical efficiency. Consideration is being given to the development of a compound whose molecules may be cross-linked to form a polymeric LB film. Another possibility is to use the polysiloxane system shown in Figure 8.2 . Such materials would be of great interest to the device specialists as they would be processible using conventional photolithographic techniques and be extremely mechanically and thermally stable.

In a practical non-linear optics device, large electric fields perturb the electron distribution within non-linear molecules and hence induce the electro-optic effect. With this in mind, modifications will be made to the surface plasmon resonance apparatus such that changes in permittivity caused by the application of an electric field will be exposed by a shift in the reflectivity resonance [124]. This will provide a convenient method of characterising the second-order non-linear optical properties of future materials which will supplement the OSHG studies.

The complexes have been shown also to possess high pyroelectric coefficients ($3.0 \mu\text{C m}^{-2} \text{K}^{-1}$) relative to other LB film materials and their large figures of merit ($0.75 \mu\text{C m}^{-2} \text{K}^{-1}$) are attracting a great deal of industrial interest for thermal imaging applications. Future work in this sphere must include the unambiguous determination of the mechanistic origin of pyroelectricity in the ruthenium complexes. Modifications to existing materials can then be made in order to improve the pyroelectric response. The ruthenium complexes synthesised in the future will form a large contribution to the development of thermal imaging devices within a major new industrial/academic research initiative.

Several novel applications of these materials other than in the non-linear physics area have arisen during the course of this work. The studies on Langmuir films described

in Chapter 5 revealed that the packing of the ruthenium molecules in monolayer and multilayer films leave large unfilled voids between the active conjugated backbones of adjacent molecules. It has been previously shown that LB films can act as efficient gas-sensing agents by adsorbing gas molecules from the ambient onto their surfaces and into their bulk. Ruthenium LB films will provide many adsorption sites because of their perforated structure. In order to detect the adsorption, several methods are feasible. The use of SAW devices proved to be an extremely sensitive method of detecting mass changes associated with adsorption [125]. The major drawback of sensors that are being currently researched is their lack of selectivity. However, different gases may change the refractive index of an LB film by varying degrees which could be measured using the SPR system. The large number of nitrile compounds, that could be modified in order to selectively respond to particular gases, can now be coupled to the ruthenium headgroup and deposited in an LB structure.

Another application of the materials developed in this work is their possible use in an optical verification device [126]. There are a wide variety of security systems for access control presently in use, the majority of which are based upon mechanical devices, magnetic strips or punched card systems. Such devices should be difficult to forge and ideally capable of remote operation. A novel security device is envisaged to consist of coloured dyes which possess extremely unique optical absorption properties rather like the coloured inks used in bank notes. The system will include sophisticated recognition electronics which will effectively measure the absorption at several wavelengths and either accept or reject the security device depending upon the agreement of the spectrum and a pre-recorded version. However, the main advantage of the proposed system, which has been recently patented, stems from the particular dyes to be used and the manner in which they will be deposited onto a substrate.

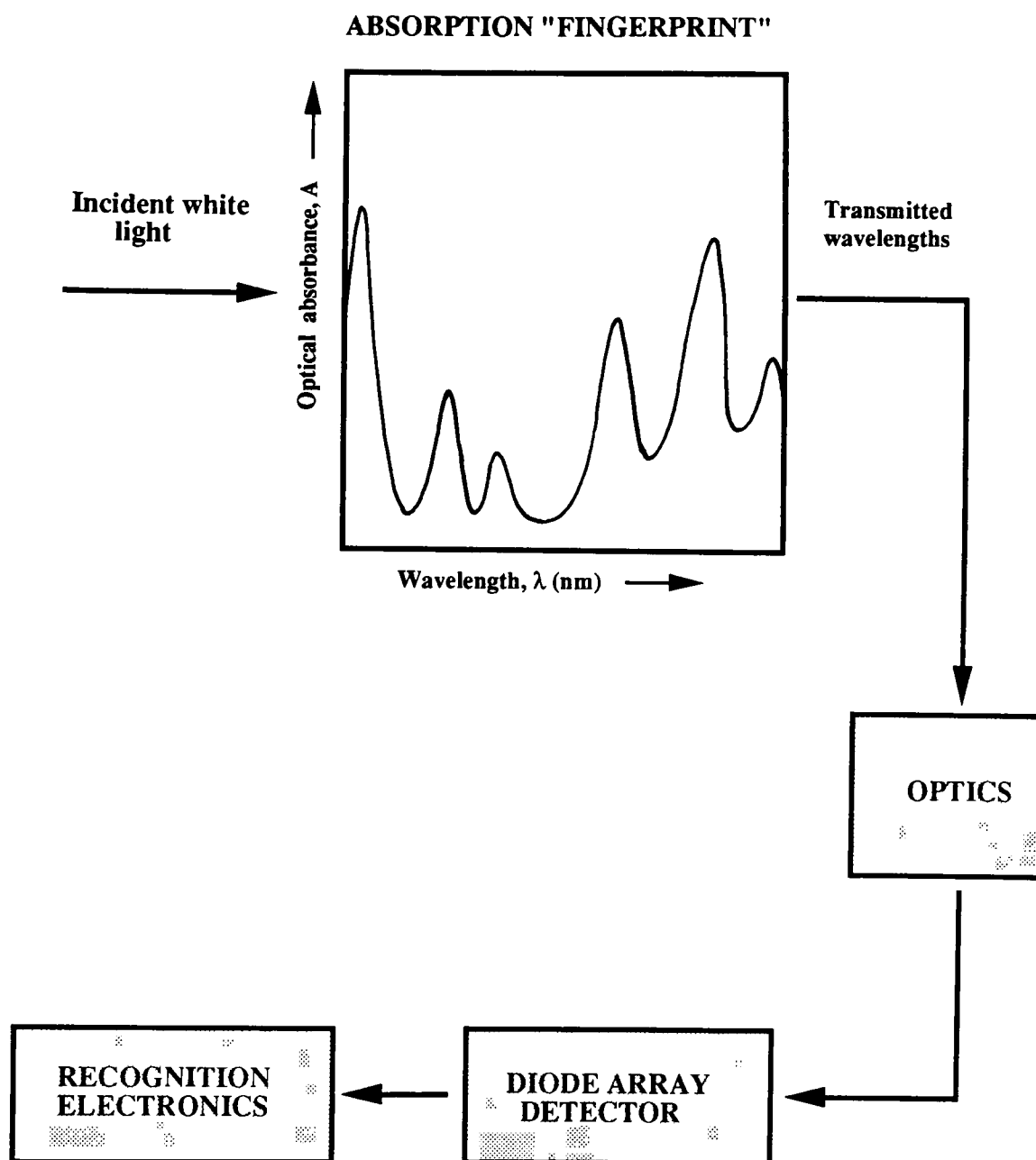


Figure 8.3 : Optical verification device system using the unique absorption properties exhibited by LB films consisting of dye and pigment molecules.

The ruthenium complexes and their precursors have been shown to possess wide-ranging transition energies which often vary depending on their molecular environment. In addition, the total observed absorbance may be precisely controlled using the LB technique. The spectral characteristics coupled to the thinness of the deposited film would produce a unique "fingerprint" for a security card which would be extremely difficult to reproduce without the availability of Langmuir trough facilities. Further security could be added using several dyes in a single monolayer and/or alternating layers of different dyes. In addition, another property of the film could be assessed such as capacitance in order to confirm the validity of the access card. This would ensure that forgery would be virtually impossible. A pictorial representation of the proposed system is included in Figure 8.3 . It is believed that the future appears promising for this application since the most unique capabilities and attributes of the deposition technique and the dye materials will be used to the full.

This thesis has described the development, preparation and characterisation of a class of novel organo-ruthenium complexes. They have been studied with the particular applications of second-order non-linear optics and thermal imaging in mind, although several other potential uses have been recognised. The research effort has consisted of contributions from chemists, physicists and materials specialists and has shown that such involvement of scientists from several different backgrounds is essential in successfully probing the mysteries of such novel and unusual materials as those described in this thesis.

APPENDIX A

Cleaning Procedures.

1. Substrates.

- (a) Glass slides
 - (i) Ultrasonic agitation in 5 % Decon 90™ solution for 30 mins.
 - (ii) Thorough rinsing in Milli-Q pure water for 30 mins.
 - (iii) Rinsing again as (ii) for a further 30 mins.
 - (iv) Reflux in propan-2-ol for 2-3 hours.
- (b) Aluminium coated glass
 - (i) If required, rinsing in propan-2-ol and blow dry.

2. Langmuir Troughs.

- (a) Trough basins
 - (i) Swill and wipe with 100 ml chloroform (Analar).
 - (ii) Rinse in propan-2-ol, allow to dry.
 - (iii) Rinse in pure Milli-Q water after drying.
- (b) Barriers and Rollers
 - (i) Rinse and wipe with acetone-soaked lint-free tissues.
 - (ii) Reflux in propan-2-ol for 2-3 hours.

3. Aluminium Evaporation.

(a) Substrate preparation

- (i) Evaporate onto clean glass slides at a rate of approximately 0.5 nms^{-1} to a thickness of 100.0 nm.

(b) Electrode deposition

- (ii) staggered evaporations following the procedure below:

1. 6 x 1.0 nm steps at a rate of 0.05 nms^{-1} .
Allow to cool for 15 mins between each step.
2. 6 x 2.0 nm steps at a rate of 0.3 nms^{-1} .
Allow to cool for 15 mins between each step.
3. 8 x 4.0 nm steps at a rate of 0.3 nms^{-1} .
Allow to cool for 25 mins between each step.
4. Total thickness of approximately 50.0 nm.

APPENDIX B

Units for Non-linear Optics.

The relationships between the "cgs/esu" system and the SI unit system yield the following conversion factors:

$$\chi^{(2)}_{\text{SI}} = 4.19 \times 10^{-4} \chi^{(2)}_{\text{esu}}$$

$$\beta_{\text{SI}} \text{ (Cm}^3\text{V}^{-2}\text{)} = 3.7 \times 10^{-21} \beta_{\text{esu}}$$

$$\beta_{\text{SI}} \text{ (m}^4\text{V}^{-1}\text{)} = 4.19 \times 10^{10} \beta_{\text{esu}}$$

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