FLOTATION OF OXIDIZED COPPER MINERALS:
AN INFRARED SPECTROSCOPIC STUDY

BY

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We accept this thesis as conforming to the
required standard

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Date April 5, 1972
ABSTRACT

Chemical and physical properties of the copper oxide surface as modified by flotation collectors have been investigated. The flotation behaviour of copper oxide minerals in the presence of anionic and cationic collectors has been studied using the Hallimond tube method. An eleven reflection, 70° incidence angle, specular reflection infrared spectroscopic technique has been employed to investigate the adsorption of carboxylic acid onto copper oxide substrates. An ATR "in situ" technique has been developed to record the spectra of the adsorbates which were present at the copper oxide/aqueous surfactant solution interface.

Micro-flotation tests indicated that mineral surface charge played the most important role in flotation of copper oxide minerals with ionic collectors. Tenorite was easily floated with an anionic collector such as lauric acid when the pH of the solution was lower than the IEP of the mineral (pH 9.4). On the other hand, lauryl amine, a cationic collector, yielded better flotation recoveries at pH values greater than the IEP.

Adsorption experiments conducted using the highly sensitive specular reflection spectroscopic technique suggested that mineral surface charge was the major variable affecting adsorption of aqueous lauric acid onto copper oxide substrates. Therefore, a relationship between floatability, surface charge and adsorption was established. The infrared spectroscopic studies showed that adsorption of collector species did not occur at pH values above the IEP. Qualitative and quantitative analyses of the spectra indicated that, at pH values below the IEP, chemi-
sorption of laurate ions as counter ions in the internal part of the electrical double layer was the predominant adsorption mechanism responsible for collection. In addition, the adsorption of monomeric lauric acid molecules, probably by hydrogen bonding to the substrate, was also observed. In the presence of excess copper ions, cupric laurate and monomeric lauric acid–copper complexes were physically adsorbed on the chemisorbed film.

Effects of molecular orientation on specular reflection spectra were analyzed on the basis of existing optical theories. The qualitative interpretation of the infrared reflection spectra of carboxylic surface species required the recording of a series of reference spectra. These included specular reflection spectra of films formed by condensing lauric and stearic acid from the vapour phase onto copper oxide and gold substrates. Standard quantitative references were obtained by transferring solidified monolayers of stearic acid from the air/water interface to the substrates according to the Langmuir-Blodgett method. Remarkable effects of molecular orientation were observed in the reflection spectra of the films mentioned above. These effects were in agreement with the predictions of the Francis and Ellison theory. In addition, these studies contributed to the understanding of the behaviour of organic monolayers on solid and liquid surfaces.

A thin film of cuprous oxide on an infrared transparent ATR prism was used as adsorbent and infrared spectra of the compounds present at the cuprous oxide/aqueous lauric acid interface were recorded "in situ". Results of these tests indicated that the composition of the adsorbed carboxylic films was not altered to any significant extent by the removal of the substrate from the aqueous phase.
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To my wife, my gratitude for her patience and understanding.
CHAPTER I
INTRODUCTION

1.1 Statement of the Problem

Non-sulphide copper ores are usually referred to as "oxidized copper ores". Many copper prospects show the presence of oxidized copper minerals along with underlying sulphides. Around the world, there are several large and small deposits of these minerals. The two basic carbonates, malachite (\(\text{CuCO}_3(\text{OH})_2\)) and azurite (\(\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2\)) are the most abundant oxidized copper minerals. The oxides of copper, cuprite (\(\text{Cu}_2\text{O}\)) and tenorite (\(\text{CuO}\)), and one group of silicates, chrysocollas, are also frequently found. Phosphates, sulphates, chlorides and other water-soluble copper salts occur in a small number of deposits.

A large majority of oxidized copper ores is treated by hydro- or pyrometallurgical processes, along, or in combination with flotation. While direct flotation, requiring low capital investment, would be an attractive method, especially for small deposits, it has in most cases been ineffective and therefore uneconomic. Froth flotation is a process to separate solid particles from each other in an aqueous pulp by selective attachment of particles to gas bubbles. The bubbles rise to the surface carrying the selected particles which are removed
in a froth while the other particles remain suspended in the pulp. With a few exceptions, minerals are completely wetted by the aqueous phase. In order to make them capable of adhering to the gas bubbles, it is necessary to change their surface characteristics from hydrophilic to hydrophobic. Collectors are used for this purpose. They are organic species which, once attached to minerals, provide them with a non-polar, hydrocarbon-like (hydrophobic) surface. The mineral industry today makes widespread use of this process to concentrate metal sulphides. On the other hand, only a small but increasing fraction of the non-sulphide minerals is concentrated by flotation.

Most of the earlier research on flotation of oxidized copper minerals has been of an empirical nature. As a result, the surface chemistry of the system flotation collector/oxidized copper mineral is far from well understood. A better knowledge of the basic phenomena of adsorption of collectors onto oxidized copper minerals is the starting point for a more logical approach to the study of recovery of these minerals by flotation. It is to this end that the research associated with this thesis is directed.

1.2 Literature Review

(a) Flotation of Oxidized Copper Minerals

The concentration of oxidized copper minerals by flotation has been the subject of much research in recent years (1-59). A great variety of methods has been proposed for floating these minerals but not many have advanced beyond the laboratory stage. Flotation of most oxidized copper minerals is difficult. There is as yet no successful
process for industrial flotation of chrysocollas. Direct flotation of ores containing carbonaceous or ferruginous gangue gives poor results because of the non-selectivity of collection. Clay mixed with the minerals prevents flotation entirely. Prior desliming may permit successful flotation of malachite and azurite ores. In some cases, treatment of the pulp with flocculants such as acrylic acid polymers may be used as a substitute for the desliming step (43,56). Long chain carboxylic collectors such as oleic acid \((\text{CH}_3\text{CH}_2)_7\text{CH=CH(CH}_2)_7\text{COOH})\) or their salts (soaps), in the pH range of 8 to 10.5, give good recovery of malachite and azurite but mediocre recovery of cuprite and tenorite. Sulphydryl compounds are also effective collectors for the carbonates of copper but excessive amounts of these reagents are required for good recoveries if used alone. Sulphidization (using \(\text{Na}_2\text{S, H}_2\text{S or molten sulphur})\) can reduce collector consumption. However, the amount of sulphidizing agent is critical; a slight excess leading to lack of floatability. Hence, stepwise sulphidization is becoming the standard procedure (53,55).

Few investigators have attempted to explain the physical and chemical mechanisms involved in flotation of oxidized copper minerals. Most of the work has been carried out on copper carbonates and silicates, in the presence of complex reagents like unsaturated fatty acids, xanthates and sulphides. The studies by Burkin and Halsey (25) and by Ivanovskii (34) are exceptions. In the former, the adsorption of lauryl amine \((\text{C}_{12}\text{H}_{25}\text{NH}_2)\) on cupric, nickel and zinc oxides was studied and it was found that the free energies of adsorption are of the same order of magnitude as those expected for the formation of the corresponding
amine complexes in solution. Therefore, formation of insoluble metal-amine complexes at the mineral surfaces was postulated. In the latter, it was shown that organic compounds used in chemical analysis to precipitate copper ions also have definite collecting properties on flotation of cuprite and chalcopyrite (CuFeS₂). Floatability of these minerals was correlated with the solubility of the copper-collector complexes.

The Use of Collectors Alone

In 1935, Rey (5) studied the fatty acid and soap flotation of malachite at pH's 8 to 9.5. He concluded that collection results from interactions of the acid with the mineral particles; the soaps act mainly as frothers.

Gaudin and Schuhmann (1936) (7) investigated adsorption of xanthates on carbonate minerals and observed that collector films adsorbed on malachite were easily removed from the surface on treating the mineral with organic solvents. They were the first to associate the difficulty in floating oxidized copper minerals with the lack of adhesion of the collector coating.

Peterson and collaborators (1965) (38) recommended the use of octyl hydroxamate as collector for chrysocolla and suggested pH 6 as the optimum flotation pH. An adsorption mechanism proposed by them shows the interaction of collector with the mineral surface as resulting from negative hydroxamate ions being adsorbed on positive copper hydroxide sites (CuOH⁺ formed at the surface of the mineral). Calculated bulk concentration of CuOH⁺ ions yielded a maximum at pH 6.0 to 6.2.
The Action of Sulphidizing Agents

In 1938, Rehbinder and collaborators (10) noticed that the treatment of malachite with sulphides lead to a decrease of surface wettability by water droplets in air.

Shorsher (16), in 1949, showed that sulphidization reduced by several times the amount of xanthate necessary for good recovery of malachite but excessive residual amounts of sodium sulphide in solution decreased the adsorption of collector and suppressed flotation.

Mitrofanov and co-workers (1955) (17) studied the kinetics of sulphidization and adsorption of xanthates and dithiophosphates on oxidized lead and copper minerals, by means of radiometric methods. An increased rate of collector adsorption after sulphidization was obtained. They observed also that sulphide films formed on malachite and chrysocolla peeled off under the abrasive action of particles in an agitated flotation pulp. In addition, they explained depression (decrease in floatability) in the presence of excessive concentrations of sulphide ions by competitive adsorption of collector and hydro-sulphide ions (HS⁻) at the surface of the minerals.

In 1956, Leja (19) investigated the floatability of malachite with xanthates and carboxylates, before and after sulphidization, and noticed again the poor adhesion of collector films. He suggested an explanation for this phenomenon based on the assumption that the surface of malachite is formed essentially by carbonate and hydroxyl groups, with copper atoms underlying them. When collector or sulphide ions establish a strong bond with the underlying copper atoms, copper diffuses out, weakening the structure of the mineral. Also, on the basis that
dissolved copper ions react with collector outside the interface, preventing particle-collector interaction, he proposed that sulphide ions activate (improve flotation of) malachite not directly on the surface but rather in the solution by precipitating copper ions. In apparent contradiction to this latter hypothesis, Pryor and Lowe (1956) (20) measured changes in copper solubility during flotation of malachite with xanthates and observed that complete flotation occurred only when dissolved copper exceeded a certain minimum concentration. This minimum amount of dissolved copper was much higher than the amount expected from the published values for the solubility product of the copper xanthates.

Abramov (1969) (52) explained the weak adhesion of collectors to the surface of lead and copper carbonates as a result of the highly hydrophilic nature of the surface of these minerals. The collector coating (metal xanthate and dixanthogen, identified by X-ray diffraction and IR spectroscopy) is porous and unable to prevent penetration of water underneath the hydrophobic films. Such weakly bonded films are easily destroyed by the action of the air bubbles causing flotation failures. Abramov believes that the main effect of sulphidization is to increase the hydrophobic nature of the mineral sublayer, making possible stronger adhesion of collector coatings, and consequently, better flotation recoveries.

The Effect of pH

Bowdish and Chen (1963) (31) reported better flotation recoveries of chrysocolla with xanthates in the pH range of 4 to 6.
In 1965, Wright and Prosser (37), using infrared and ultraviolet spectroscopic techniques, identified cuprous xanthate together with dixanthogen and cupric sulphide as the products of the reactions of chrysocolla and malachite with xanthate in the presence of sodium sulphide. They explained the flotation behavior of chrysocolla on the basis of the relative positions of these products and a silica gel layer formed during the reactions. According to their model, flotation is possible near pH 5 because only under this condition does precipitation of the reaction products occur at the surface of the minerals.

In 1970, Bowdish and Plouf (54) observed that the negative surface charge of chrysocolla shows an unexpected increase as pH decreases from 6.0 to 4.5. They explained this behavior by assuming that in this pH range the incipient leaching of copper from the mineral is higher which gives the surface a less negative potential. They correlated this phenomenon with increasing sulphide adsorption and flotation recovery.

**Summary**

It is apparent from the above review that no satisfactory correlation exists among the various theories proposed. The author believes that in order to understand such complex flotation systems, it would be beneficial to examine the mechanisms of adsorption of simple collector species on copper oxides. This requires a general discussion on the theories of adsorption and charge formation on oxide surfaces.
Mechanisms of Collector Adsorption

Surface chemists classify adsorption as either physical or chemical. This classification is purely relative and does not characterize the real nature of the phenomena (60). "Physical" adsorption can be caused by van der Waals forces (weak forces due primarily to induced polarization resulting from instantaneous dipoles created by electronic motion) or by other weak forces such as long range coulombic attractions, hydrogen bonding,* charge-dipole, dipole-dipole and induced dipole interactions. In this type of adsorption, the adsorbate maintains its chemical identity. "Chemical" adsorption (or "chemisorption") is due to strong interatomic forces (covalent or ionic). It is more selective and leads to formation of monomolecular layers only. Chemisorbed monolayers are more properly called "surface compounds" (2,3). One interesting characteristic of the surface compounds is that their chemical and physical properties do not always coincide with the properties of existing bulk compounds. Peck and Wadsworth (61), obtained direct evidence of formation of surface compounds by means of infrared spectroscopy.

The mechanisms most often used to explain adsorption of flotation collectors on mineral surfaces (1-4, 62,63) are summarized in Table 1. Collector adsorption phenomena frequently involve more than one mechanism. Lateral van der Waals attraction between non-polar chains of the collector species may also play a role in the mechanism by strengthening adsorption.

* Somewhat strong hydrogen bonds may be formed between the adsorbent and the adsorbate. The phenomenon, in this case, is more often classified as chemical adsorption.
Table 1. Classification of the Mechanisms of Collector Adsorption.

A. As neutral molecules:
   i. Physical adsorption on top of previously adsorbed collector species (multilayer formation).
   ii. Physical adsorption at the mineral surface (monolayer).
   iii. Chemisorption due to strong hydrogen bonding.
   iv. Surface compound formation by chemical reaction between collector molecules and surface groups. The reaction product can be:
      iv.a. a surface compound for which analogous species are known to exist in the bulk state, or
      iv.b. a surface compound for which no analogous compounds have ever been isolated.

B. As ionic species:
   i. Precipitation of surface compounds (solubility theory of flotation).
   ii. Adsorption as counter ions in the double layer (ion adsorption theory):
      ii.a. physical adsorption in the external part of the double layer,
      ii.b. physical adsorption in the internal part of the double layer, or
      ii.c. chemical adsorption in the internal part of the double layer.
Adsorption of Neutral Molecules

In Table 1, Class A mechanisms describe the interactions of mineral surfaces with uncharged collector species. Flotation collectors are in most cases ionizable compounds. But neutral molecules, in the form of undissociated collector or neutral products of reactions involving collector species, are likely to be present in the flotation systems and may be adsorbed at the mineral surface. The real significance of adsorption of neutral collector species to the flotation process is not known. Some investigators believe that in many cases chemisorption of collectors in their neutral forms (mechanisms A.iii. and A.iv.) is the predominant phenomenon leading to mineral collection. Although physically adsorbed molecules (mechanisms A.i. and A.ii.) are commonly present in collector coatings, their role in the flotation process has been assumed of secondary importance compared with that of the chemisorbed species (61).

Solubility Theory of Flotation

The "solubility theory" (mechanism B.i., Table 1) was suggested by Taggart and associates (64), in 1930. This theory assumes that adsorption of collectors on minerals is due to chemical bonds which obey laws closely related to those governing the precipitation of substances of low solubility. Crystal structure, surface electrical properties and physical adsorption phenomena are usually disregarded by this theory. The differentiation between this mechanism and mechanism A.iv.a. is often difficult in practice. Existing analytical tools, usually, do not enable one to decide whether adsorption occurs by the reaction of unionized collectors at the mineral surface or by an ion
precipitation mechanism.

Many examples exist showing a close relationship between solubility of metal-collector complexes, adsorption of collector on minerals and flotation. Du Rietz (65) published a series of solubility data for carboxylic acids and their salts and stressed its importance as a guide in selecting adequate flotation conditions. Part of his data is reproduced in Appendix A, together with other solubility data for carboxylic compounds most pertinent to the present work.

Based on the solubility theory and on the possibility of formation of very stable surface complexes, chelating agents were suggested as collectors for the flotation process. Chelating agents are molecules which have more than one active group capable of coordinating with a metallic ion to form a ring-like structure, usually very stable. The use of chelating agents in flotation of oxidized copper minerals has been proposed by several investigators (11-13,15,34,38).

**Ion Adsorption Theory**

In 1955, Gaudin and Fuerstenau (66,67) introduced the fundamentals of the so-called "ion adsorption theory" (mechanisms B.ii.a., B.ii.b., and B.ii.c., Table 1). Its contribution to the understanding of the mechanisms of flotation, especially flotation of oxide and silicate minerals has been outstanding. According to this theory, the driving force for adsorption of collectors on minerals is primarily coulombic in nature; i.e., collector ions are attracted to oppositely charged surfaces by electrostatic forces. Further discussion of the ion
adsorption theory requires the knowledge of the structure of the 
"electrical double layers".

Figure 1 is a schematic representation (Stern model) of the 
electrical double layer (1,60). It shows a spherical particle in an 
aqueous solution and the potential drop across the interface. Five 
zones can be differentiated: the solid particle zone (AB), the layer 
of potential-determining ions (BC), the layer of anchored counter ions, 
known also as internal or Stern layer (CD), the aqueous layer containing 
counter ions, called the external or Gouy-Chapman layer (DE) and the 
bulk liquid (EL). The potential drop across the double layer can be 
divided into two parts: $\psi_0 - \psi_\delta$, the linear drop across the Stern layer 
and $\psi_\delta$, the exponential drop across the diffuse layer. The potential 
$\zeta = \psi_\delta$ is called the electrokinetic or zeta potential. If a particle 
such as the one shown in Fig. 1 is placed in an electric potential 
gradient, the solid and its surroundings to the left of plane P 
(shear plane) will move in one direction and the liquid to the right 
will move in the opposite direction. The zeta potential is the potential 
at the shear plane. It is related to measureable parameters such as 
electrophoretic mobility, streaming potential, sedimentation potential 
and electroosmotic pressure. Techniques for evaluating $\zeta$ are discussed 
elsewhere (1,60,68).

The ion adsorption theory states that collector ions function as 
counter ions in the double layer. The adsorption of ions in the 
diffuse layer (mechanism B.i.i.a., Table 1) is physical in nature. 
Adsorption in the Stern layer can be physical or chemical, according 
to the strength of the adsorbate/adsorbent bonds. Besides electrostatic
Figure 1. The electrical double layer.
attractions, electrostatic repulsions between ions, lateral van der Waals forces, hydrogen bonds and covalent forces are likely to participate in the mechanisms of adsorption of flotation collectors in the Stern layer. In the case of mechanism B.ii.b., i.e., physical adsorption in the Stern layer, the distance of approach of the adsorbed ions to the surface is relatively large and consequently electrical attractions are weaker. This mechanism is highly non-selective. Also, any decrease in the concentration of collector ions in solution leads to a proportional decrease in the amount of collector physically adsorbed at the mineral surface. This is not always true in the case of chemisorption of ions (mechanism B.ii.c.) which involves much closer distances of approach of adsorbate to the surface. Strong electrostatic attractions are developed and depending on chemical affinities, other bonds (covalent or hydrogen bonds) can reinforce the collector/surface group interactions. Solubility of the surface compounds and steric effects become important; the adsorption process is more selective.

(c) Charge Formation on Oxide Surfaces

The potential-determining ions have a major influence in the mechanisms of the ion adsorption theory since they determine the sign and magnitude of the mineral surface charge. In the case of ionic solids, the ions constituting the crystal lattice are the most important potential-determining ions. The surface charge of oxides is highly dependent on the pH of the solution, and the role of hydrogen and hydroxyl ions (H\(^+\) and OH\(^-\)) as potential-determining ions in the case of
oxide surfaces is well recognized. According to Parks (69), surface charge formation on oxides can be explained by the following mechanisms:

Oxide surfaces in an aqueous environment are hydroxylated. Charge can be formed on these surfaces by dissociation of the hydroxide group:

\[
\begin{align*}
\text{MOH} & \leftrightarrow \text{MO}^- + \text{H}^+ \quad (I) \\
\text{MOH} & \leftrightarrow \text{M}^+ + \text{OH}^- \quad (II) \\
\text{M}^+ + \text{H}_2\text{O} & \leftrightarrow \text{MOH}_2^+ \quad (III) \\
\text{MOH} + \text{H}^+ & \leftrightarrow \text{MOH}_2^+ \quad (IV)
\end{align*}
\]

(M represents a metal atom at the oxide surface).

Acid dissociation (reaction I) produces negative sites. Reactions II, III, and IV produce positive sites. Also, charged hydroxo-complexes derived from dissolution of the solid are expected to be specifically adsorbed and act as potential-determining ions. Adsorbed positive complex ions form positive surface sites and negative complex ions form negative sites. Adsorption of these potential-determining ions is proportional to their concentration in the solution which in turn depends on pH. The pH at which the net surface charge of an oxide is zero was designated as the isoelectric point (IEP) or the point of zero charge (PZC). Later, Parks (70) differentiated these terms stating that:

"If charge is established only by H\(^+\), OH\(^-\), and species capable of interacting with H\(^+\), OH\(^-\), and H\(_2\)O to form species present in the solid lattice, i.e. by potential-determining ions (PDI), then the PZC may be conveniently given the special name of IEP\((s)\)."
More recently Parks and Smith (1969) (71) redefined the terms PZC and IEP. The PZC was considered as the pH at which equal adsorption of \( \text{H}^+ \) and \( \text{OH}^- \) should lead to zero surface charge. The pH at which the observed zeta potential is equal to zero was named the IEP. PZC and IEP are identical only when no specific adsorption of charged hydroxo-complexes occurs. (This last nomenclature will be followed throughout this dissertation.)

**IEP of Cupric Oxide**

The IEP of cupric oxide has been measured at pH 9.4 ± 0.4 (69). The solubility diagram for cupric oxide (Fig. 2) shows that the IEP is approximately equal to the pH at point P where equal concentrations of \( \text{CuOH}^+ \) and \( \text{Cu(OH)}_3^- \) should be present in the bulk solution. This seems to indicate that the equilibrium constant of the acid and basic dissociation reactions of the hydroxylated copper surface sites are equal to those of analogous bulk reactions leading to the formation of the hydroxo-complexes \( \text{CuOH}^+ \) and \( \text{Cu(OH)}_3^- \). The point P is also at the pH where the calculated solubility of cupric oxide is minimum. According to Parks and deBruyn (72), the pH of minimum solubility should coincide with the IEP only in the absence of specific adsorption of hydroxo-complexes. If this is the case, \( \text{OH}^- \) and \( \text{H}^+ \) should be the main potential-determining ions of cupric oxide and the concentration of copper ions in solution should not affect the position of the IEP of the system.
Figure 2. Solubility diagram for CuO and Cu(OH)$_2$ (from ref. 81).
IEP of Cupric Hydroxide

Yoon and Salman (73) studied the effect of pH on the zeta potential of cupric hydroxide (Cu(OH)$_2$, a metastable compound formed by basic precipitation of copper ions in water*) and found the IEP of freshly prepared samples at pH 7.7. The IEP of dry aged hydroxide containing superficial cupric oxide was found at pH 7.3. The solubility diagram for CuO and for Cu(OH)$_2$ (Fig. 2) shows the lines for Cu$^{++}$ ions derived from the hydroxide and from the oxide intercepting the OH$^-$ line at pH's 7.8 and 7.4, respectively (points P1 and P2 in the diagram). Based on this fact, they concluded that Cu$^{++}$ and OH$^-$ are the major potential-determining ions of cupric hydroxide precipitates.

1.3 Scope and Approach of the Study

The purpose of the present work has been to investigate the mechanisms of adsorption of collectors onto copper oxide substrates and their relationship with the floatability of the oxidized copper minerals.

Experimentally, the project has consisted of two main phases: (i) flotation studies and (ii) infrared spectroscopic studies. The results of these experiments have been used to interpret the role of mineral surface charge in the mechanisms of adsorption of collector onto copper oxide substrates.

* Diagrams of equilibria in systems containing copper, water, oxygen, carbon dioxide and sulphur are presented in Appendix B.
The Role of Mineral Surface Charge on Tenorite Flotation

Single mineral micro-flotation tests* have been carried out on tenorite to investigate the significance of surface charge on the floatability of this mineral with ionic collectors. In so doing, the role in the flotation of tenorite played by H\(^+\) and other ions which are likely to be specifically adsorbed on oxidized copper surfaces has been examined. Since this stage has established a correlation between surface charge and flotation recovery, it was then of prime interest to investigate the effect of surface charge on the adsorption of collector species onto oxidized substrates.

Adsorption of Aqueous Lauric Acid onto Copper Oxide Substrates

In searching for the relationship between surface charge and adsorption of collector, the interfacial reactions of copper oxides in aqueous solutions of lauric acid (C\(_{11}\)H\(_{23}\)COOH) have been studied. The effect of variables such as pH, collector concentration, cupric ions concentration, partial pressure of carbon dioxide, dissolved oxygen concentration, time of exposure and circulating velocity of the liquid, on the nature and concentration of the adsorbed laurate species, has been investigated. To avoid side reactions which could preclude the interpretation of the adsorption mechanisms, the systems studied have been made as simple as possible. Lauric acid, a straight chain, saturated carboxylic (fatty) acid was the collector selected. It is a powerful collector with relatively simple chemistry. Highly pure, artificial oxides of copper (cupric and cuprous oxides) were used as

* Laboratory flotation tests on the scale of a few grams sample are commonly called micro-flotation tests.
adsorbents. During reaction, the liquid phase containing known concentrations of reagents was kept in an all teflon vessel under closely controlled gaseous environments.

Surface reaction products and adsorbed films have been analysed by infrared (IR) spectroscopy. The recording of IR spectra of thin surface films requires the use of unconventional, highly sensitive, spectroscopic techniques (74,75).* "Reflection spectroscopy" (76) makes use of optical arrangements to force the radiation to pass through one film several times, increasing sensitivity. The following reflection spectroscopic techniques have been used in the present studies:

(i) Multiple Specular Reflection Technique

An eleven reflection, 70° incidence angle technique has been applied to the studies of adsorption of lauric acid onto copper oxide substrates. This technique has made possible identification and quantitative appraisal of adsorbed collector species at surface concentration levels as low as one-third of a monomolecular layer ("monolayer"). Concentrations lower than one-tenth of a monolayer have been detected. Previously, this and similar systems had never been analyzed with such a high degree of sensitivity.

Successive monolayers of stearic acid (C_{17}H_{35}COOH) were deposited onto copper oxide coated front surface gold mirrors according to the "Langmuir-Blodgett method" and their specular reflection spectra were recorded. The purpose of these experiments has been to establish

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* A general discussion of the theories and applications of these techniques is presented in Chapter II.
standard reference spectra for quantitative analysis of the carboxylate species adsorbed on copper oxide substrates from aqueous solutions. Reflection spectroscopy still is, essentially, a relative method of analysis. Absolute measurement of adsorbate concentration or average film thickness, directly from IR band intensity, is not possible at this stage of advance of the reflectance theories. Valuable quantitative information can be gained by comparing sample spectra with the spectra of films of known concentration or known thickness. Films with known concentrations of fatty acids can be built by transferring compact monolayers of the acid from the liquid/air interface to the solid surface (Langmuir-Blodgett method) (77).

A series of experiments have been conducted to investigate the effects of molecular orientation on the IR spectra of surface films recorded by the specular reflection technique.* These have included the recording of spectra of stearic acid molecules deposited onto gold and copper oxide substrates, from the gaseous phase and from the air/water interface. Films with molecules presenting different degrees of orientation were formed by deposition on smooth and rough substrates.

(ii) "In situ" Attenuated Total Internal Reflection Technique

"In situ" infrared spectra of carboxylic compounds adsorbed on copper oxide films have also been recorded. Specular reflection techniques require the extraction of the adsorbent from the aqueous

* This subject may seem to bear little relationship to the main objectives of the present work. However, the author believes that the results of these experiments may be of special use to the development of the theories of reflection spectroscopy and the understanding of the behavior of organic monolayers at solid surfaces and at liquid/gas interfaces. For this reason, these experiments will be described and discussed at full length in the present dissertation.
medium prior to recording of the spectra. Since there was a possibility that this procedure might have altered the composition of the interfaces, a technique for recording "in situ" IR spectra of cuprous oxide surfaces has been developed. This technique was based on the principles of attenuated total internal reflection spectroscopy (ATR) (78). Spectra of the substrate, the interface and portions of the bulk aqueous medium were recorded simultaneously.

* Attempts to record "in situ" spectra of cupric oxide films failed because of lack of adhesion of the oxide to the IR transparent materials.
CHAPTER II
INFRARED SPECTRA OF SOLID SURFACES

2.1 Transmission Technique

Conventional Spectroscopy

It has been said that one of the most characteristic properties of a compound is its infrared spectrum.

Infrared light covers the wavelength range of 0.8 to 2000 μ (one micron = 1 μ = 10^{-6} cm). The infrared spectrum is divided into the regions: the "near infrared" which is the region between 0.8 and 2.5 μ; the "mid-infrared" between 2.5 and 50 μ; and the "far infrared" which lies between 50 and 100 μ. The term infrared spectroscopy conventionally denotes the study of absorption spectra in the mid-infrared region.

Infrared light is also described in terms of wavenumbers; i.e.,
\[ \nu = \frac{1}{\lambda} \text{ cm}^{-1}, \]
where \( \lambda \) is wavelength in centimeters. The wavenumber range of conventional infrared spectroscopy is 4000 to 200 cm^{-1}.

The recording of intensity of the IR radiation transmitted through (or absorbed by) a sample versus frequency yields a curve showing absorption bands characteristic of the atoms and chemical bonds present in the sample. This is the absorption infrared spectrum as obtained by conventional transmission infrared spectroscopy. Absorption bands that appear in a range characteristic for a certain group and that are
useful for identification of that group are called characteristic frequencies. Appendix C contains characteristic group frequencies for compounds most closely related to the present work.

Beer's Law and Absorption Parameters

Absorption band intensities are related to the concentration of the absorbing species. According to Beer's law, the intensity of light $I$, transmitted at wavenumber $v$ by an absorbing medium is given by:

$$ I = I_0 e^{-k_v cl} \tag{1} $$

where $I_0$ = intensity of incident radiation; $c$ = concentration of absorbing molecules in the sample; $l$=path length of light in the sample; and $k_v$ = "absorption coefficient" (characteristic of the absorbing species in the sample).

The transmittance $T$ is defined as $I/I_0$. Another quantity, the absorbance $A$, is defined as:

$$ A = \varepsilon_v' cl \tag{2} $$

where $\varepsilon_v'$ is an "extinction coefficient" expressed in mole$^{-1}$liter.cm$^{-1}$ ("molar extinction coefficient" = $\varepsilon_v$) or in molecule$^{-1}$cm$^{-1}$ ("molecular extinction coefficient" = $\varepsilon_v$).

A "mass absorption coefficient" $\alpha_v$, also used in association with Beer's law, is defined as:
\[ \alpha_v = 2.303 \frac{A}{l} \]  \hspace{1cm} (1 \text{ in cm}) \]  \hspace{1cm} [3]

or \[ \alpha_v = 2.303 \rho \times \varepsilon_v \]  \hspace{1cm} (\rho \text{ = density in molecule.cm}^{-3})[4]

The absorption characteristics of a compound can be expressed by still another constant \( K \) (unitless), called "absorption constant" and defined by the relation:

\[ K = \frac{\alpha \lambda}{4\pi} \]  \hspace{1cm} [5]

where \( \lambda \) is the wavelength in centimeters.

Difficulties in Recording IR spectra of Thin Surface Films

Conventional transmission IR spectroscopy is of limited application to studies of adsorbed species or thin films of reaction products formed on solid surfaces. This is due to the following reasons:

(i) Most solids present very strong absorption bands in the IR region which confines the absorption bands belonging to surface species to a rather limited spectral range.

(ii) Solid particles may scatter a significant amount of energy which is then lost, reducing instrument performance.

(iii) Absorbance of thin surface layers is usually extremely low.

To counteract these effects there are two practical ways of increasing absorbance by the surface species and decreasing radiation absorption or scattering by the substrate. One, the powder method, uses high area samples to increase the available surface for adsorption.
and to decrease radiation scattering by reducing the particle sizes below the wavelength of the IR light. The other, the reflection method, will be the subject of Sections 2.2 and 2.3.

Pressed Salt Technique

In order to record the spectra of powders, one must deal with the problem of supporting the sample in the normal beam position of the spectrophotometer. There are several techniques to accomplish this. One of the most commonly used is the "pressed salt technique" in which the powder is mixed with fine crystals of an IR transparent salt and pressed in order to form a disc. The disc is easily mounted on the spectrophotometer and its IR transmission spectrum recorded. To a good approximation, band intensities obey Beer's law. A few flotation investigators have used the pressed salt technique for analysing collector films formed on oxidized copper substrates (37,52,79,80). However, care must be exercised in the interpretation of spectra of surface films obtained by this technique. Changes in the character of the surface may be produced by the pressing process (81). Ion exchange reactions between the surface species and the salt matrix may occur (82). Also, IR transparent salts usually absorb a fair amount of atmospheric water. The presence of water in the sample makes difficult the assignment of bands due to surface species in the IR spectral regions close to the characteristic absorption bands of water (given in Appendix C). For these reasons, the pressed salt technique was used in the present work only for recording spectra of bulk solid compounds (reference transmission spectra). Surface films were analyzed by means of reflection techniques.
Figure 3. Optical arrangement for reflection spectroscopy. (Multiple reflection attachment manufactured by Wilts Scientific Corp. Model 9).

Figure 4. Variation of n and k through an absorption band.
2.2 Multiple Specular Reflection Technique

If radiation passes through a thin layer of a light absorbing material located on a highly reflecting metal surface, a plot of reflectance against frequency constitutes a specular reflection spectrum of the material. Usually, a pair of mirrors covered with the film to be analyzed is employed and an optical arrangement forces the radiation to pass through the film several times (as illustrated in Fig. 3). Multiple reflection spectroscopy is of particular interest to studies of physical and chemical interactions of molecules with the solid surfaces. In a recent review of the technique, Poling concluded that although there are some discrepancies among the theoretical analyses of the optical phenomena involved, they all confirm that:

1. recording infrared reflection spectra of films as thin as one monolayer can be achieved with the use of commercial dispersive type spectrophotometers;

2. reflection spectra of moderately absorbing films such as organic films differ very little in appearance from transmission spectra;

3. information on molecular orientation in anisotropic films can be gained from the spectra;

4. band intensities can often be related directly to average film thickness" (83).

Position, Shape and Intensity of Reflectance Bands

A "reflectance band", i.e. a removal of energy from the reflected radiation, is produced by two interrelated phenomena: (a) an increase in the absorption coefficient (k) of the absorbing medium; (B) a decrease in the refractive index (n) of the medium near the absorption band (84).
Typical variations of $n$ and $k$ through an absorption band are shown in Fig. 4. The extent of the dispersion in the refractive index is proportional to the variation in the value of $k$. For a moderately absorbing film (maximum $k$ values of approximately 0.1; e.g., organic films) the dispersion in the value of $n$ is small. Phenomenon A is mainly responsible for the formation of the reflectance band which, in this case, has shape and position coinciding with those of an absorption band (as obtained by transmission spectroscopy). For the case of very high values of $k$, the dispersion in $n$ is appreciable and band formation is governed by phenomenon B. Reflectance bands of strongly absorbing films are expected to resemble the dispersion in the refractive index. Consequently their shape and position should differ from absorption bands.

In reflection studies, band intensities are usually measured in terms of $\Delta R$; fractional change in reflectivity at a band maximum:

$$\Delta R = \frac{R - R_0}{R_0}$$

where, $R_0 = \text{reflectivity in the absence of a film}$, and $R = \text{reflectivity at band maximum}$.

For the case of multiple reflections, a spectrophotometer, linear in transmittance, will record $T = R^N$ and $T_0 = R_0^N$ ($N$ is the number of reflections) from which $\Delta R$ values can be calculated ($T_0 = \text{transmittance or reflectance in the absence of a film}$, and $T = \text{transmittance or reflectance at band maximum}$).

The minimum $\Delta R$ value which can be measured depends on the number of reflections employed. Using seven reflections, $\Delta R$ values as low
as 0.0005 have been measured reproducibly (85). For a higher number of reflections, even lower values can be obtained. However, Greenler (86) has shown that there is an optimum number of reflections for each incidence angle. His results indicate that the optimum number of reflections varies from 8, for 88° incidence, to 25, for 70° incidence. A decrease in sensitivity of the order of 20 to 30 percent is obtained by using half the optimum number of reflections.

Francis and Ellison Theory

Among the various attempts to explain the IR reflection spectra of thin films on metal surfaces, the work by Francis and Ellison (87) deserves special mention. Based on Fry's treatment of the absorption of radiation by a thin isotropic film on a reflecting surface (88), their theory predicts that absorption of the component of radiation perpendicular to the plane of incidence would not be detectable. The fractional change in reflectivity of the parallel component (ΔR//) would be given by the following expression:

\[
\Delta R// = \frac{16\pi d \cos \theta}{\lambda} \left[ \frac{n_{1} K_{1} \sin^{2} \theta}{n_{1} \cos^{2} \theta} - \frac{n_{4} f(n_{1}, \theta)}{K_{4}^{3} \cos \theta} \right] \tag{7}
\]

where (see Fig. 5a), d is the film thickness, \(\lambda\) is the wavelength, \(\theta\) is the angle of incidence, \(n_{1}\) and \(n_{4}\) are the refractive indices of the film and of the metal, respectively, \(K_{1}\) and \(K_{4}\) are absorption constants, and \(f(n_{1}, \theta)\) is a function of \(n_{1}\) and \(\theta\) which has a value of the order of magnitude of unity.
5(a) Reflection from a filmed metal.

\[ \delta = 180^\circ; E_1 = 0 \text{ at surface} \]

5(b) Phase shift (\( \delta \)) during reflection component normal to the plane of incidence.

\[ \delta = \text{small}; E_{//z} = \]

5(c) Parallel component. Finite phase shift. Standing wave field \( E_{//z} \) normal to the metal surface.

Figure 5. Francis and Ellison Theory.
For good reflectors and values between 0° and 80°, \( K_4^3 \cos^4 \theta \gg n_4 \) and the approximation \( \frac{n_4 f(\theta)}{K_4^3 \cos^4 \theta} \to 0 \) can be made. Equation [7] can then be simplified to a more practical form:

\[
\Delta R// = \left[ \frac{16 \pi \sin^2 \theta \frac{K_4}{3}}{\lambda \cos \theta n_1^3} \right] \times d \quad [8]
\]

A thin film cannot absorb the component of the radiation perpendicular to the plane of incidence because of the fact that this component undergoes a near 180° phase shift during reflection for all angles of incidence. As illustrated in Fig. 5b, a standing wave is formed having zero amplitude at the surface. Consequently, no interactions with the oscillating dipoles of the absorbing species at the surface can take place. The same is not true for the parallel component (Fig. 5c) which undergoes a finite phase change on reflection, but this becomes 180° only at 90° incidence angle. The parallel component gives rise to a standing wave field \( E//,z \) directed mainly normal to the plane of the reflecting surface. Since only this component can interact and be absorbed by the film, installation of an IR polarizer, oriented to eliminate the "ineffective" perpendicular component from the radiation reaching the detector of the instrument, markedly enhances the percentage absorption of the parallel component of the light.

**Effects of Molecular Orientation**

The preceding discussion applies to films in which there is no molecular orientation. For the case of films having anisotropic optical
properties, an analysis of the behavior of their IR spectra, based on the aforementioned work by Francis and Ellison, is presented below.

The intensity of a spectroscopic transition (as given by any of the absorption parameters defined earlier) is directly related to the probability $P$ that a molecule (or group) will undergo a transition in unit time. For good reflectors at incidence angles between $0^\circ$ and $80^\circ$, $P$ can be approximated by the following expression:

$$P = \frac{4\pi}{h^2} \mu_z^2 E_{//,z}^2$$  \[9\]

where, $h$ is Planck's constant, $\mu_z$ is the component (perpendicular to the metal surface) of the matrix element of the dipole moment for the transition, and $E_{//,z}$ is the "effective" electric field at the molecule (or group).

Molecular orientation should not strongly affect the component of the field perpendicular to the surface (the only component of the light which can be absorbed by the film). Anisotropy, however, should affect the components of the matrix element of the dipole moment. If the molecules (or groups) in the film are oriented with respect to the reflecting surface, the dipole moment changes will have a specific direction for each vibrational mode. Since the field will be predominantly perpendicular to the surface, only $\mu_z$ will be effective in producing absorption of radiation. Vibrational modes in surface species producing dipole moment changes parallel to the surface will appear abnormally weak in the spectra of films on metal mirrors.
Francis and Ellison reported experimental results which confirmed their theoretical predictions. They recorded the spectra of metal stearates deposited as solidified monolayers on metal mirrors using the Langmuir-Blodgett technique. Four reflections and a 72° incidence angle were employed. Sensitivity for recording spectra of films one monolayer thick was obtained. In the deposited layers, the methylene groups lie in planes nearly parallel to the surface. Stretching vibration bands assigned to these groups were unusually weak. Asymmetric and symmetric stretching vibrations of oriented carboxylate groups have dipole moment changes nearly parallel and normal to the surface, respectively. Bands assigned to the former mode were abnormally weak; the latter produced relatively intense bands.

Spectra of Copper Oxide Films

Poling (85) recorded IR specular reflection spectra of copper mirrors subsequent to oxidation in air, at moderately high temperatures. Seven reflections and an incidence angle of 73° were used. The intensities of the copper oxide bands were directly proportional to film thickness (0 to 900 Å) as determined by an interferometer. For mirrors oxidized at a temperature of 140°C, the only band detected was an intense band at 640 cm$^{-1}$. Transmission spectra of bulk cuprous and cupric oxides exhibit single bands at approximately 620 and 510 cm$^{-1}$, respectively (see Appendix C). The oxide film grown on these mirrors was identified as relatively pure cuprous oxide (Cu$_2$O). The +20 cm$^{-1}$

* Wieder and Czanderna (89) reported that instead of Cu$_2$O, an oxide phase of composition Cu$_{0.67}$O$_{0.33}$ is formed in thin copper films (200 to 2400 Å thick) by heating in oxygen atmosphere.
shift of band position, due to dispersion of the refractive index, agreed with that calculated by means of equation [8] and using K and n values given by O'Keefe (90). Mirrors oxidized at temperatures above 250°C produced spectra containing a single band at 560 cm$^{-1}$, thus the films were identified as cupric oxide (CuO). The 560 cm$^{-1}$ band maximum for cupric oxide represents a +50 cm$^{-1}$ shift from the position of the absorption band.

Greenler and co-workers (84) reported the reflectance band for Cu$_2$O (or CuO$_{0.67}$) at 655 cm$^{-1}$. They employed an optical accessory which produced one to three reflections and a spread of the incidence angles from 84° to 90°. Film thickness of 450, 900, 2500, and 4200 Å were analysed. Band intensity increased with film thickness to a maximum at a thickness of 2500 Å then decreased on a further increase in film thickness.

Spectra of Collector Films Adsorbed on Copper Substrates

Leja and associates (91) applied the multiple specular reflection technique to analysis of xanthate species adsorbed from aqueous solutions onto oxidized and sulphidized copper substrates. They identified the spectra of the chemisorbed xanthate as that of cuprous xanthate. Formation of multilayers of cuprous xanthate and dixanthogen was also deduced.

Low and co-workers (92) recorded specular reflection and emission spectra of the products of reaction of oleic acid with copper plates (various degrees of oxidation), in air, and at temperatures varying from 27 to 300°C. Their results suggested that the main product of the
reaction is a binuclear copper oleate complex: $[\text{R-COO}^-]_4\text{Cu}^{++}\cdots\text{Cu}^{++}$. A small band formed at 1735 cm$^{-1}$ was assigned to an ester-like species:

```
\[ \begin{array}{c}
0 \\
\text{Cu-O-C-R} \\
0 \\
\text{Cu} \\
0-H \\
\end{array} \]
```

Paterson and Salmon (80) also observed a very minor band at 1735 cm$^{-1}$ during studies of absorption of aqueous sodium oleate on cupric hydroxide, using the pressed salt technique. Eischens (93) reported the presence of similar "ester" species during chemisorption of acetic acid (CH$_3$-COOH) on silica and SiO$_2$-MgO catalysts. His spectra showed the C=O stretching band of the supposed "ester" at 1747 cm$^{-1}$. A band at 1389 cm$^{-1}$, associated with the "ester" was attributed to bending vibrations of the CH$_3$ groups. However, as pointed out by Eischens, "no attempt was made to confirm this interpretation by a study of chemisorbed dueterated acetic acid." (93)

Scowen and Leja (94) published IR specular reflection spectra of films adsorbed on oxidized copper substrates from aqueous sodium laurate ($10^{-4}$ to $10^{-3}$ M solutions) at various pH's. Their spectra were recorded using a six reflection, 45° incidence angle technique. At neutral pH, they reported that sodium laurate was adsorbed on thickly oxidized copper; a mixture of sodium and cupric laurate was adsorbed on slightly oxidized copper; and for a vacuum deposited film, the species was cupric laurate. In acidic solutions, the adsorbed species was cupric laurate. At pH's $>9$, no adsorption was detected.
2.3 Attenuated Total Internal Reflection Technique

Theory and applications of ATR spectroscopy have been summarized in a book by Harrick (78). The familiar phenomenon of total internal reflection is shown in Fig. 6a. The radiation is totally reflected from the interface of a transparent dielectric prism (refractive index \(n_1\)) and a medium of lower refractive index (\(n_2\)) at angles greater than \(\theta\) critical (\(\theta_c = \sin^{-1}n_2/n_1\)). During total internal reflection, the radiation penetrates slightly into the rarer medium. The penetrating electric field (evanescent wave) can interact and be absorbed by the rarer medium or any thin film of light absorbing material placed on the face of the dielectric prism. The ATR spectra of the rarer medium and the film (if present) are obtained by plotting reflectance versus frequency. The position and shape of the ATR bands are similar to those of transmission absorption bands. The sensitivity of the technique is highly increased by using multiple reflections as illustrated in Fig. 6b.

"In situ" ATR

With the advent of ATR spectroscopy in 1959 (95), the hopes for recording "in situ" IR spectra of aqueous liquid/solid interfaces were revived. The procedure normally followed during spectroscopic (transmission or specular reflection) studies of surface films formed at water/solid interfaces is to record spectra of the solid before and after exposure to the solution. This is a consequence of the fact that the water IR spectrum usually presents very broad absorption bands.
6(a) Total internal reflection

6(b) Multiple ATR prism

6(c) "In situ" ATR

Figure 6. Attenuated total internal reflection spectroscopy (ATR).
Path lengths greater than a few microns in the aqueous medium are sufficient to block most of the IR spectral region. The extraction of the solid from the solution is undesirable because it might alter the chemistry of the interfaces and intermediates might not be observed.

The extent of penetration of the evanescent wave into the rarer medium depends upon parameters such as the angle of incidence, the matching of refractive indices, the wavelength, and polarization. It can be made to vary from practically zero to several microns. It is the possibility of limiting the penetration of the radiation into an aqueous (rarer) medium, which makes ATR a potential technique for "in situ" IR spectroscopic studies.

Previous "in situ" ATR Studies

(i) Ultraviolet and Visible Region

Hansen and co-workers (96) and Srinivasan and Kuwana (97) used a glass-prism coated with tin oxide for recording "in situ" ultraviolet-visible ATR spectra of compounds formed during electrochemical reactions between the tin oxide film and an electrolyte. A similar technique has been employed for simultaneous electrochemical and visible spectroscopic studies on thin films of platinum (98) and gold (99) deposited on glass.

(ii) Infrared Region

Mark and Pons (100) used an "in situ" ATR technique for observing IR spectra of organic species formed at a germanium prism electrode during electrolysis. In their technique the adsorbent was the IR transparent prism. The recording of "in situ" IR spectra of adsorbed
species using thin films of light absorbing material as the adsorbent (such as a prism coated with a cuprous oxide film, employed in the present work and shown schematically in Fig. 6c) has not been reported.
CHAPTER III
EXPERIMENTAL METHODS

3.1 Flotation Tests

Introduction

Single mineral microflotation tests were carried out with a modified version of the cell proposed by Hallimond (101,102) and known as the Hallimond tube. The selection of this microcell was made on the assumption that reproducibility of experimental parameters is easier with this device than with other known laboratory microcells. The widespread use of the Hallimond tube and its modifications in laboratory flotation investigations would also allow more direct comparison with reported data.

Tenorite was floated using lauric acid, lauryl amine, oleic acid and amyl xanthate, under different pH conditions. The effect of ions which might be specifically adsorbed by oxidized copper surfaces, e.g. carbonates, sulphides and cupric ions, was investigated. Lauric acid, \( \text{C}_{11}\text{H}_{23}\text{COOH} \rightarrow \text{C}_{11}\text{H}_{23}\text{COO}^- + \text{H}^+ \), and lauryl amine, \( \text{C}_{12}\text{H}_{25}\text{NH}_2 + \text{H}^+ \rightarrow \text{C}_{12}\text{H}_{25}\text{NH}_3^+ \), were selected to represent the anionic and cationic family of collectors, respectively. The main purpose of using oleic acid and xanthate as collectors was to obtain microflotation data which could be compared with plant practice or with previous laboratory results.
(a) **Materials**

**Mineral**

The copper oxide used was analytical grade cupric oxide manufactured by Fisher Scientific, Co. (Cat. No. C-474). This material comes in the form of "wires"; e.g. cylindrical geometry of approximately 0.5 mm diameter and 5 mm long. These wires were stage ground in an agate mortar, then dry screened with the −48 to +100 mesh fraction being separated for the flotation tests. The flotation samples assayed 82.4% copper, compared with the theoretical values of 79.8% and 88.8% Cu for tenorite and cuprite, respectively. Minor impurities were specified as 0.002% carbonates and less than 0.004% sulphates. X-Ray diffraction showed that the samples contained tenorite as the predominant mineral and cuprite as a secondary component. The diffraction pattern, showed no other lines besides those of the oxides. The IEP of this tenorite sample was measured at pH 9.4, using Mular and Roberts method (103) (see Appendix D).

**Collectors**

The lauric acid used was 99.5% pure (gas-liquid chromatography) supplied by K & K Laboratories, Inc. Lauryl amine and oleic acid were of a purified grade obtained from Chem. Service, Inc. The xanthate used was a laboratory grade potassium amyl xanthate, purified by successive dissolution in acetone and recrystallization in ether.

**Modifiers**

Analytical grade sulphuric acid and sodium hydroxide were employed for pH control. The other reagents used; sodium sulphide and cupric
sulphate, were also analytical grade.

**Water**

Throughout this research solutions were prepared using double distilled water. This water, when freshly distilled showed: conductivity ranging from \(1.5 \times 10^{-6}\) to \(1.9 \times 10^{-6}\) ohms \(^{-1}\) cm \(^{-1}\); surface tension higher than 70.0 dynes cm \(^{-1}\) and pH varying from 6.5 to 6.9. Water conductivities were determined using a conductivity meter manufactured by Radiometer Copenhagen (type CDM 2d). Surface tension was measured by the drop-volume method (104). A Beckman Zeromatic SS3 pHmeter, provided with a probe combination electrode (Beckman 39183) was used for pH determinations. Before each test the electrode was standardized with solutions buffered at pH's 4.01, 7.00 and 9.18, freshly prepared at the beginning of each week. pH's were taken with a precision of \(\pm 0.05\) pH units.

**Gases**

High purity, oxygen-free nitrogen and argon were used. In order to reduce the carbon-dioxide content of these gases and consequently the pH changes resulting from its adsorption into the pulp during flotation, the gases were further purified by passing them through a gas washing bottle containing a saturated sodium hydroxide solution.

(b) **Flotation Apparatus**

The Hallimond tube employed is illustrated in Fig. 7. It is similar to that described by Fuerstenau and co-workers (105) except that the glass frit is used in place of a capillary and the flotation
Figure 7. Modified Hallimond Tube.
column is modified to prevent mechanical carry-over of non-floatable material and "hold back" of mineralized bubbles at the edge of the ground joint. The rubber stopper serves to support a combination electrode. The probe type electrode has a small (10 mm) diameter which makes possible measurements of pH inside the flotation cell. An outlet (open to air) is provided to permit the escape of gases introduced into the cell. The gaseous atmosphere above the pulp can be controlled by forming a positive pressure, gas barrier inside the cell. Selected gases are introduced into the cell through the gas inlet shown in Fig. 7. The scoop is used to place the mineral sample at the bottom of the flotation column without breaking this barrier.

The complete flotation apparatus is shown schematically in Fig. 8. It includes a gas system designed to deliver known volumes of gas to the Hallimond tube at a measurable average flow rate. This system is a simplification of the one used by Fuerstenau (106) and contains:

A - nitrogen and argon cylinders, provided with pressure regulators;

B - gas-washing bottle containing saturated sodium hydroxide solution;

C - three-way stopcock to direct gas to D, or to the flotation cell through the gas inlet supported by the rubber stopper;

D - three-way stopcock to direct gas to the burett (E), or to the cell through the glass frit;

E - burette, to measure volume of gas delivered to the cell;

F - constant water-head vessel, to maintain the gas at a constant pressure;

G - trap;

H - two-way stopcock.
Figure 8. Microflotation apparatus.
(c) Operating Procedures

Two procedures were followed during the flotation tests. In the first procedure, no attempt was made to control the gas above the flotation pulp. In the second, an argon barrier was maintained above the liquid to minimize diffusion of atmospheric gases, containing carbon dioxide, into the pulp.

**Procedure I:** No attempt to prevent diffusion of atmospheric carbon dioxide into the pulp. The sequence of steps is described below.

1. Thirty cm$^3$ of nitrogen gas was introduced into the burette and kept at a pressure of approximately 60 cm of water. This pressure provided an average gas flow through the cell of 0.5 cm$^3$.sec$^{-1}$, as estimated in separate tests.

2. The upper half of the Hallimond tube (part above the ground joint) was removed and the sample to be floated (two grams of -48 to +100 mesh tenorite) was placed into the cell.

3. The two halves of the tube were then rejoined and clamped.

4. 100 ml of solution containing the flotation reagents were prepared in a graduated cylinder. When required, the solution was heated to a temperature slightly below 50°C, to speed dissolution of the collector. The solution was brought to a temperature of 25±1°C and its equilibrium pH (initial pH = pH$_i$) was measured.

5. The reagent solution was transferred from the graduated cylinder to the cell through the upper opening of the tube. The pH electrode was then immersed in the liquid by inserting the rubber stopper in the opening.
6. The magnetic stirrer was turned on. The pulp was conditioned for five minutes after which the pH was again measured (conditioning pH = pH\textsubscript{c}). The stirrer had been pre-set to the minimum velocity necessary to keep the solids in suspension.

7. The 30 cm\textsuperscript{3} of gas stored in the burette was then forced to flow through the Hallimond tube. Bubbles were formed at an average flow rate of 0.5 cm\textsuperscript{3}\textpersec (one minute flotation time).

8. The final pH (pH\textsubscript{f}) was read. The average of pH\textsubscript{c} and pH\textsubscript{f} was considered as the flotation pH (pH\textsubscript{r}).

9. The flotated fraction, collected in the "concentrate" stem, and the non-floated material, remaining on top of the glass frit, were individually removed from the cell, dried at 80°C and finally weighed on an analytical balance.

---

**Procedure II: Minimization of the diffusion of carbon dioxide into the pulp.**

This procedure is essentially the same as that described in Procedure I except for the use of argon gas instead of nitrogen, preparation of reagents and introduction of the mineral sample to be floated.

The solution containing reagents was prepared in the following manner. Carbon dioxide content of the double distilled water was lowered by boiling and by bubbling argon in a narrow necked flask. The water was then cooled to approximately 50°C, the reagents were added, and this solution cooled further to 25°C. During this time, bubbling of argon was maintained.

At this stage, 100 ml of the reagent solution was poured in the
Hallimond tube as described previously. Argon was introduced into the cell through the glass frit and a further argon purging of the solution started inside the flotation cell. The rubber stopper was placed on the tube. The scoop containing the mineral sample was kept above the liquid. Argon was also introduced into the cell through the gas inlet of the rubber stopper. The purpose of this was to maintain a positive argon pressure to act as a barrier between the liquid and the atmospheric gases. The argon barrier was maintained up to the end of step 8 (Procedure I). The purging of the solution lasted approximately thirty minutes after which pH was measured. Then, by sliding the scoop into the liquid, the sample was placed on the bottom of the flotation column. Steps 6 to 9 were carried out as described in the previous procedure.

3.2 Infrared Spectroscopic Studies

Introduction

Transmission reference spectra of copper oxides, cupric hydroxide, malachite, cupric laurate, sodium laurate, lauric acid and stearic acid were recorded using the potassium bromide disc (pellet) technique (107).

Mirrors for the specular reflection spectroscopic studies were pairs of quartz slides coated with a reflecting metal film (vacuum-evaporated gold film). A film of copper oxide on top of the reflecting metal or the gold itself were used as substrates for adsorption studies. The reflection spectra of carboxylic surface films, formed by various methods, were analysed by comparison with transmission reference spectra of similar bulk compounds or with reflection spectra of films of known
composition. Hence, some specular reflection studies were conducted with the unique purpose of facilitating the assignment of IR bands associated with carboxylic surface species.

Samples prepared for "in situ" ATR studies of adsorption of lauric acid onto cuprous oxide substrates were composed of KRS-5 (thallium bromide-iodide) prisms coated with a thin film of the oxide. The presence of strong water bands in the IR spectra obtained using "in situ" techniques makes rather difficult the assignment of weak bands, associated with adsorbed surface species, and located in the vicinity of the strong bands. In order to overcome this problem, "in situ" spectra were recorded using $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$ as aqueous media.*

3.2.1. Materials

Evaporation sources

Oxygen-free high-conductivity (OFHC) copper chips, contained in a molybdenum dimpled boat were employed as the evaporation source during vacuum-deposition of copper films. Cominco gold bullion (99.999%) in splatter form, also contained in a molybdenum boat, was used as the source for evaporated gold substrates.

Carboxylic Surfactants

High purity *stearic acid* manufactured by Chem Service, Inc. was employed. Measurements of the surface pressure of monolayers of this acid, spread at the air-water interface of a Langmuir trough (see Appendix F), gave pressure-area curves analogous to those given in the

* The molecules of $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$ absorb the IR light in quite distinct spectral regions (see table of characteristic frequencies given in Appendix C). The purpose of the alternative use of these media was to expand the IR region available for recording spectra of thin surface films.
literature (77), confirming the high purity of the material. Lauric acid was of the same quality as that used during the flotation tests (already discussed in Section 3.1, p. 42). Sodium laurate was obtained by neutralization of lauric acid solutions with sodium hydroxide and was purified by recrystallization from ethanol. Cupric laurate was prepared by precipitation from solutions of lauric acid in the presence of cupric sulphate, followed by rinsing with water, washing with acetone, and drying under vacuum.

Organic Solutions

Carbon tetrachloride, normal hexane, acetone, and ethanol were all spectrophotometric grade reagents.

H$_2$O and D$_2$O

The properties of the double distilled water used throughout this work have already been described in Section 3.1, p. 43. Deuterium oxide containing 99.82% D$_2$O was supplied by Atomic Energy of Canada Ltd.

pH Regulators

Analytical grade sulphuric acid, sodium carbonate, bicarbonate and hydroxide were employed for pH control.

Gases

High purity compressed air and argon were used after passing them through a gas washing bottle containing saturated sodium hydroxide solution to reduce carbon dioxide contaminations. Analysed gas mixture
of carbon dioxide in nitrogen (295 ppm CO₂) was supplied by Canadian Liquid Air Ltd.

**Oxidized Copper Minerals**

Malachite was an analytical grade basic cupric carbonate supplied by Fisher Scientific Co. (C 453). Cupric oxide was obtained by heating this malachite for 30 hours at 280°C, in air. Certified grade cuprous oxide (Fisher C 477) was used after it had been washed with acetone to remove the pine oil preservative. Cupric hydroxide was precipitated from copper sulphate solutions by neutralization with sodium hydroxide. The precipitate was rinsed with double distilled water, filtered and dried under vacuum.

**Miscellaneous Chemicals**

Infrared quality potassium bromide crystals were employed as the matrix material of the pressed discs.

All the other chemicals used were of a certified grade.

3.2.2 **Sample Preparation**

(a) **Potassium Bromide Discs**

Discs for transmission spectroscopy were prepared by mixing 1 mg of the sample material with 500 mg of potassium bromide in an agate mortar; transferring the mixture to a die (Perkin-Elmer Model 186-00251); evacuating for 5 minutes; and pressing for 3 minutes at 5000 psi. The discs were 16 mm in diameter and approximately 1 mm thick.
Copper Oxide Coated Front Surface Gold Mirrors

Cupric and cuprous oxide substrates were prepared for the IR specular reflection spectroscopic studies according to the following procedure:

1) The quartz slides (57 x 20 x 3 mm and 44 x 20 x 3 mm thick; optically flat surfaces) were carefully cleaned by soaking in warm detergent solutions; rinsing with boiling water; degreasing in freshly prepared chromic acid (potassium dichromate added to concentrated sulphuric acid); thoroughly rinsing with boiling water; and drying at temperatures over 100°C.

2) Gold films (370 Å thick*) were vacuum deposited on a pair of slides using the resistive-heating, thermal evaporation technique (108). Thickness of the films was a critical factor. Thicker films showed a tendency to peel off in aqueous media especially after exposure to temperatures above 200°C. On the other hand, thinner films presented poor reflectivity in the long wavenumber IR region (4000 to 2500 cm⁻¹). For this reason the following evaporation procedure had to be followed closely: clean slides were placed at a distance of 20 cm from the source; the unit was evacuated to 10⁻⁸ torr; and 260 ± 10 mg of gold were evaporated by applying a fixed voltage to the source which permitted complete evaporation of the metal in three minutes.

* Film thickness was measured within ± 30 Å using a multiple beam interferometer (Angstrometer, SLOAN model M-100, marketed by Sloan Instrument Corp.).
3) A metallic copper film (200 to 250 Å thick) was deposited on top of the gold film. The evaporation procedure adopted was analogous to that described in Step 2 above except that the distance from the slide to the source was 25 cm instead of 20 cm, and 65 ± 5 mg of copper were evaporated. After the deposition of the copper film, the samples were removed from the vacuum chamber and stored in an argon gas environment.

4.i) Cupric oxide coated front surface gold mirrors were formed by oxidizing the copper films, in an oxygen atmosphere, at 240 ± 5°C, for approximately 15 hours. The mirrors were cooled to ambient temperature before their spectra were recorded. The thickness of the oxide films varied from 340 to 420 Å (measured by interferometry). Analysis of the cupric oxide films formed on top of gold by transmission electron-diffraction showed that the oxidized films were composed essentially of cupric oxide. The electron-diffraction patterns contained no other rings besides those characteristic of CuO (and of the gold underneath). Pictures (Fizeau interference fringes and transmission electron micrograph) showing the topography of the cupric oxide front surface mirrors are presented in Fig. 9.

4.ii) Cuprous oxide (or CuO$_{0.67}$) films were formed by oxidation of the copper films at 140 ± 5°C, in the presence of oxygen, for 6 hours. Films 320 to 400 Å thick were produced. Transmission electron-diffraction patterns confirmed that the oxidized films contained cuprous oxide as the predominant component. However, weak rings assigned to cupric oxide were also observed.
9(a) Fizeau interference fringes of a typical cupric oxide substrate (front surface gold mirrors; the oxide has been coated with a thin gold film). Taken with the multiple beam interferometer: fringe-to-fringe spacing = 2945 Å; 15 x horizontal magnification.

9(b) Transmission electron-micrograph of a cupric oxide surface (acetate replica).

Figure 9. Surface topography of cupric oxide substrates.
Smooth and Rough Gold Substrates

Smooth gold surfaces were prepared by carrying out only the first two steps of the procedure used for production of copper oxide front surface gold mirrors given above. The gold mirrors were removed from the vacuum chamber after completion of Step 2 and stored in an argon environment. Transmission electron-diffraction was used to analyse the gold films and confirmed their high degree of purity. Interferometric fringes (Fig. 10a) and an electron micrograph (Fig. 10b) are presented to illustrate the flatness of the surface of these mirrors.

Rough gold substrates were obtained by depositing films of the metal on rough quartz surfaces. Immersion of the optically flat quartz slides in a 48% solution of hydrofluoric acid for 15 minutes yielded surfaces with the desired degree of roughness (surface depressions approximately 1000 Å deep). The procedure followed for evaporation of these gold films was similar to that used during preparation of smooth gold mirrors except that in this case thicker films (2000 Å) were deposited. The formation of thicker films was required to insure that surface depressions were completely filled and no quartz was exposed at the surface. The degree of roughness of the surface of these mirrors is illustrated in Fig. 11.

(II) Deposition of Carboxylic Films

Adsorption from Aqueous Solutions

Adsorption of lauric acid from aqueous solutions onto copper oxide or gold substrates was conducted in an all-teflon reaction vessel under
10(a) Fizeau interference fringes of a typical gold mirror (smooth surface) (fringe-to-fringe spacing = 2945 Å; 15 x horizontal magnification).

10(b) Transmission electron micrograph of a smooth gold surface (acetate replica).

Figure 10. Surface topography of smooth gold substrates.
11(a) Fizeau interference fringes of a rough surface gold mirror. (fringe-to-fringe spacing = 2945 Å, 15 x horizontal magnification).

11(b) Transmission electron micrograph of a rough gold surface (acetate replica).

Figure 11. Surface topography of rough gold substrate.
controlled gaseous atmosphere and at constant temperature (25 ± 1°C). The procedure involved dissolution of lauric acid in warm (less than 50°C) double distilled water, outside the reaction vessel, in a 500 ml teflon bottle. Approximately 300 ml of the solution was transferred to the reaction vessel which was then immersed in a constant temperature bath. pH regulators and other reagents were added. Fig. 12a shows schematically the arrangement inside the reaction vessel at this stage. The selected gas was continuously bubbled through the solution to ensure saturation. Solutions of lauric acid in D₂O were prepared similarly.

In order to avoid possible contamination of the system, introduced by the pH meter combination electrode, pH measurements were made outside the reaction vessel. With the help of a hypodermic syringe, small (10 ml) samples were taken from the solution at regular time intervals and placed in a separate container for pH checks. When gases containing carbon dioxide were used, bicarbonate and carbonate of sodium were added as pH regulators in order to allow faster equilibria of the gas-solution system.

After reaching the equilibrium pH, the level of the solution was adjusted to 200 ml (using the syringe) and the substrate (pair of mirrors) was immersed in the liquid. Fig. 12b shows the inside of the vessel at this new stage. A flow of the gas was maintained above the solution during the reaction. Agitation was provided by means of a magnetic stirrer.

At pre-established time intervals, the mirrors were removed from the liquid, washed with double distilled water which had been pre-adjusted
a. Arrangement inside the vessel before reaction (equilibrium pH not attained yet)

b. Arrangement inside the vessel during reaction.

Figure 12. Adsorption of aqueous lauric acid onto mirrors. All teflon reaction vessel.
to approximately the same pH value as the solution and dried under an argon jet. Infrared spectra of the samples were recorded immediately after the drying step.

The mirrors were again immersed in the solution, following the recording of the spectra, when a longer exposure to the reagents was required. In this case, the solution was kept under constant gas purging during the spectroscopic measurements.

Monolayers Deposited from the Langmuir Trough

A teflon coated Langmuir trough (77,109) (3 liters capacity) was used for the transfer of solidified stearic acid monolayers from the air-water interface onto gold (smooth and rough) and cupric oxide substrates, according to the Langmuir-Blodgett method. The trough was provided with a wax-coated aluminum floating barrier (teflon ribbon closing the gap) and a mechanically operated, moveable teflon barrier. A torsion wire balance was employed for the measurement of forces; one degree rotation of the torsion head corresponded to a surface pressure of about 0.21 dynes cm$^{-1}$.

The trough was filled with a $10^{-4.5} \text{N} \text{H}_2\text{SO}_4$ solution ($\text{pH} = 4.4 \pm 0.2$). Following cleaning of the liquid surface by sweeping with barriers, and sucking up contaminants with a small clean tube attached to a suction pump, a pair of mirrors (slides fully covered with the substrate material) were immersed in the water. A monolayer of stearic acid was then formed on the liquid surface by spreading the acid with a volatile

* Calibration curve for the torsion wire is given in Appendix E.
water-insoluble solvent (hexane). This monolayer was compressed and
the relationship between the surface pressure and the area occupied by
the molecules of the film was established. *

After solidification of the monolayer, the mirrors were drawn up
through the monolayer covered liquid surface while the surface pressure
of the film was kept constant at $27 \pm 1$ dyne.cm$^{-1}$. In so doing, part
of the solidified monolayer was transferred to the mirror surfaces.
For all the monolayers transferred throughout this work the measured
decrease in the area of the film remaining in the trough (area of the
film transferred to the mirrors) was equal, within $\pm 2\%$ estimated experi-
mental error, to the geometric area of the mirrors (transfer ratio =
$1.00 \pm 0.02$). In view of the fact that the transfer ratio of solidified
monolayers for quartz may be different from the ratios for gold and for
copper oxide substrates (110), mirrors used in connection with this
method were covered on both sides by substrate.

The mirrors were withdrawn from the water with their longer edges
in the horizontal position and their larger faces at an angle of 45°
with the liquid surface. The rate of withdrawal was 0.5 mm.min$^{-1}$.

Once a first layer was deposited and its spectrum recorded, multi-
layers were built up by lowering and raising the mirrors through the
filmed liquid surface. **

All the films were deposited at room temperature which varied from
20 to 25°C.

* See Appendix F for typical pressure-area curve obtained.
** Multilayers built in this way contained an odd number of "alternative
layers" of the fatty acid molecules (111); the acid molecules in layers of
odd number were oriented in the opposite direction to those in layers
of even number, as shown below:

odd number layers: \[ \text{hydro-carboxylic heads carbon tails} \]
even number layers: \[ \text{carbon} \]
Films Condensed from the Vapour Phase

Lauric and stearic acid thin films were deposited onto gold and cupric oxide substrates by heating the acids in open air and condensing their vapour onto the mirrors. No attempt was made to quantize the deposition parameters. The substrates were located at approximately 10 cm above the source and were exposed to the vapour for a few minutes. The samples were stored under an argon environment and their spectra were recorded at pre-established intervals of time.

After deposition of organic films, some samples were treated with organic solvents in order to investigate the solubility and strength of adhesion of the adsorbed films. This procedure was applied also in the case of films formed in aqueous solutions or deposited by the Langmuir-Blodgett method.

(c) ATR Samples

A copper film was vacuum deposited onto the larer face of a 52.5 x 20 x 2 mm thick, 45° face angles, KRS-5 prims (cleaned in acetone) and then oxidized to cuprous oxide. A procedure, analogous to steps 3 and 4.ii used for formation of cuprous oxide front surface gold mirrors, was followed during evaporation and oxidation of the copper film.

Lauric acid solutions (2 x 10^-5 M, in H_2O or D_2O) were prepared in a teflon bottle under argon purging and placed in a constant temperature bath.
3.2.3 Recording the Spectra

Instrument

Infrared spectra were recorded on a Perkin-Elmer, model 521, double-beam, grating spectrophotometer. This spectrophotometer permitted the recording of differential spectra from 4000 to 250 cm\(^{-1}\) on a percent transmission mode, at expansions up to 20X.

The whole optical system was kept under a constant dry-air purge. The sampling area was covered with a plexiglass box (see Fig. 13) provided with sliding doors on top. This allowed easy manipulation of samples and reflection accessories without exposing the unit to large volumes of atmospheric air containing water vapour. Dry-air purging reduced the intensity of interfering bands resulting from the presence of residual water vapour in the unbalanced arms of the optical system. It was particularly useful during expanded scale operations. The dry-air was supplied by an oilless compressor fitted with zeolite filled drying columns.

Spectra were recorded at temperatures (measured in the sampling area of the instrument) varying from 25 to 33°C.

(a) Transmission Spectra

Spectra of sample discs were recorded differentially against pure potassium bromide reference discs.

(b) Specular Reflection Spectra

Multiple specular reflection spectra (eleven reflections, 70° incidence angle) of sample mirrors were recorded against a reference beam attenuator. The procedure was to record spectra of the mirrors before
Figure 13. Sampling area of the spectrophotometer covered for the dry-air purge.

Figure 14. Multiple reflection attachment (Wilks Model 9) and sample holder.
and after their exposure to aqueous media.

Parallel polarization was used in all the measurements. A polarizer (Perkin-Elmer part 186-0241), placed in the common beam of the spectrophotometer, before the entrance slit of the monochromator, was employed to eliminate the component of the light perpendicular to the reflecting surfaces.

A single beam multiple reflection attachment (see Fig. 14), marketed by Wilks Scientific Corp. (Model 9; optical lay-out shown in Fig. 3) was used for transferring light from the sample beam of the source optics to the mirrors. The sample holder (also shown in Fig. 14) was specially constructed to give the mirrors a fixed position relative to the sample beam, and consequently, to provide a reproducible number of reflections and incidence angles. Spacers kept the mirrors parallel to each other, at a fixed, 2 mm, distance apart. Eleven reflections were obtained using incidence angles spreading from 64 to 76°. This arrangement made possible the detection of fractional changes in reflectivity (ΔR) of the order of 0.0001. ΔR values as low as 0.0003 were measured reproducibly within tolerance limits of ± 10%.

The presence of the sample mirrors and the reflection attachment in the path of the sample beam lowered the transmitted power level of the instrument (as measured at 2100 cm⁻¹) from 100% to 45-48%, for the case of copper oxide front surface gold mirrors; 48-52%, for smooth gold mirrors, and 38-40%, for rough surface gold mirrors.

(c) ATR Spectra

A twenty-five reflection, 45° incidence angle, ATR technique was employed. Differential spectra were recorded with internal reflector
plates in both beams of the instrument. The purpose was to obtain better compensation for the atmospheric absorption and flatter base lines. KRS-5 internal reflector plates were supplied by Wilks Scientific Corp. (cat. # 9-3004-A). Spectra of the substrate (cuprous oxide film coating the larger face of the prism) were taken before, during and after its exposure to aqueous solutions. During "in situ" measurement there were only eleven reflections from the liquid-solid interface because of the geometry of the cell confining the liquid. Spectra were recorded without polarization of the light.*

Model 9 (Wilks Scientific Corp.) multiple reflection attachments (same used for specular reflection) were inserted in the paths of the sample beam and the reference beam. The holder used for the reference prism was a Wilks MIR 1 internal reflection plate holder. The sample prism was supported by an all teflon liquid cell. The cell body has a shape similar to that of a Wilks MIR 3 liquid sample holder except that the reaction vessel was enlarged to contain 10 ml of the liquid. This volume of the lauric acid solution was introduced into the cell with the aid of a hypodermic syringe. The cell was closed to the atmosphere during recording of "in situ" spectra. For measurements made after exposure to the liquid, the samples were dried in an argon jet.

The presence of the multiple reflection attachment and the internal reflector plate (not coated) in the path of the sample beam radiation

* Preliminary tests, conducted using parallel and perpendicular polarization, failed to indicate any improvement in the quality of the spectra by the use of the polarizer (band heights were independent of polarization). On the contrary, the introduction of the polarizer decreased the total energy reaching the detector impairing instrument performance.
lowered the transmitted power level of the instrument from 100% transmission to approximately 45% (measured at 2100 cm\(^{-1}\)). Using an internal reflector plate coated with cuprous oxide, the level was lowered to 25-30% and the presence of the aqueous medium in the ATR cell ("in situ" experiments) brought this level to values as low as 15% transmission.
4.1 Flotation Experiments

(a) The Role of Mineral Surface Charge in Tenorite Flotation

Flotation tests carried out on tenorite using anionic \((2 \times 10^{-5} \text{ M lauric acid solution})\) and cationic \((2 \times 10^{-5} \text{ M lauryl amine solution})\) collectors, in the pH range of 3 to 11.5, indicated a close relationship between flotation recovery and mineral surface charge. In Fig. 15 flotation recoveries are plotted against \(\text{pH}_i\), initial pH measured in step 4 of Procedure I (Section 3.1.c). The curves intercept in the neighborhood of the IEP of tenorite (approximately pH 9.4). Lauric acid is seen to be an effective collector at pH's below the IEP, where the surface of tenorite is positively charged; lauryl amine is effective at pH's above the IEP (negative surface charge). Identical behavior has been observed for other oxide minerals in similar flotation systems (4). Investigators have interpreted the symmetry of anionic and cationic flotation curves about the IEP as a support for the ion adsorption theory (mechanisms B.ii, Table 1, Section 2.1).

In Fig. 16, the results of tenorite flotation tests conducted using lauric acid as collector, in the absence (Procedure II) and in the presence of atmospheric carbon dioxide (Procedure I) are compared.
Figure 15. Flotation of tenorite with anionic and cationic collectors (Procedure I).
Figure 16. Flotation of tenorite in the presence (Procedure I) and in the absence (Procedure II) of carbon dioxide contaminations. $2 \times 10^{-5}$ M lauric acid solutions.
Recoveries are plotted against initial pH (pHᵢ) and average flotation pH (pHᵢₑ). In the pH range 7 to 9.4, the recovery versus pHᵢₑ curve occurs at more acid pH's: 1. when carbon dioxide is present as opposed to absent; and, ii, when compared with the corresponding pHᵢ curve (carbon dioxide present). This can be assumed to be caused by fast pH drifts associated with carbonate reactions in the 7 to 9.4 pH range (as discussed in part b below). The recoveries obtained in the absence of carbon dioxide indicate that mineral collection occurs under all pH's below the IEP of tenorite, which supports the view that surface charge plays the most important role in the process.

Experimental data related to the flotation tests and illustrated in Figs. 15 and 16 are given in more detail in Tables 2 and 3, respectively. These tables also include results of "blank tests"; i.e., tests carried out with no collector present in the solution. The purpose of these tests was to evaluate the role of purely mechanical factors in the test procedures used. Very low "recoveries" (<0.6%) were obtained which indicated that particles carried over by mechanical forces made a negligible contribution to the total weight of the "concentrates".

(b) Changes in Pulp pH

The pH drifts shown in Table 2 (Procedure I, carbon dioxide present in the flotation system) suggest that chemical equilibrium was not reached in the interval of time used to condition and float the samples. Independently of the presence or absence of collector, pulp pH's presented a tendency to increase under acidic conditions and to decrease
### Table 2

Results of Flotation Tests on Tenorite (Procedure I)

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<th>pH&lt;sub&gt;f&lt;/sub&gt;</th>
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<th>pH&lt;sub&gt;f&lt;/sub&gt; (pH&lt;sub&gt;c&lt;/sub&gt;+pH&lt;sub&gt;f&lt;/sub&gt;/2)</th>
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* Recovery = 100 x weight "concentrate"/(weight of "concentrate" + weight of non-floated)

Material losses were of the order of 1% of the weight of the original samples.
Table 3

Results of Flotation Tests on Tenorite (Carbon Dioxide Contamination Minimized; Procedure II)

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<th>( \text{pH}_c )</th>
<th>( \text{pH}_f )</th>
<th>( \text{pH Drift} )</th>
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<td>10.00</td>
<td>9.95</td>
<td>-0.15</td>
<td>9.975</td>
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<tr>
<td>9.95</td>
<td>9.85</td>
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<td>-0.10</td>
<td>10.50</td>
<td>1.9</td>
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under basic conditions. A qualitative explanation for this behavior can be put forward on the basis of the following arguments:

(i) Dissolution of cupric oxide is primarily responsible for the pH increases in the acidic media. At pH's below the IEP, the hydrolysis of cupric oxide proceeds according to reactions which tend to increase the pH of the solution, as for example:

\[
\begin{align*}
\text{CuO} + \text{H}_2\text{O} & \rightleftharpoons \text{Cu}^{++} + 2\text{(OH)}^- \\
2\text{CuO} + 2\text{H}_2\text{O} & \rightleftharpoons \text{Cu}_2(\text{OH})_2^{++} + 2\text{(OH)}^- \\
\text{CuO} + \text{H}_2\text{O} & \rightleftharpoons \text{Cu(OH)}^+ + \text{(OH)}^-
\end{align*}
\]

The higher solubility of cupric oxide in acidic water is indicated by its solubility diagram (Fig. 2).

(ii) The pH drifts in basic media are due mainly to reactions of carbonate ions (formed by adsorption and hydrolysis of carbon dioxide from the air) with the cupric oxide surface and its hydrolysis products. These reactions lead to the formation of basic cupric carbonate (malachite) as suggested by thermodynamic data (see Fig. B3, Appendix B). The equilibria of the carbon dioxide hydrolysis reactions

\[
\begin{align*}
\text{CO}_2(\text{gas}) & \rightleftharpoons \text{CO}_2(\text{aq}) \\
\text{CO}_2(\text{aq}) + \text{H}_2\text{O} & \rightleftharpoons \text{H}_2\text{CO}_3
\end{align*}
\]
\[ \text{H}_2\text{CO}_3 \quad \leftrightarrow \quad \text{HCO}_3^- + \text{H}^+ \]

\[ \text{HCO}_3^- \quad \leftrightarrow \quad \text{CO}_3^{2-} + \text{H}^+ \]

(equilibrium diagram presented in Appendix B, Fig. B4) are changed in a manner to favour the left to right reactions during formation of malachite because of the consumption of carbonate ions (\(\text{HCO}_3^-\) of \(\text{CO}_3^{2-}\)). The overall pH dependence of these reactions can explain the decrease in pH of a basic pulp.

In the absence of carbon dioxide (see Table 3) the pH drifts in acidic media were dictated by the hydrolysis of cupric oxide. In basic media, the pH drifts were insignificant and probably related to other phenomena such as adsorption of potential determining ions and collector dissociation reactions.

(c) **Effect of Sulphide Ions**

Addition of sulphide ions to the pulp expanded the pH range of floatability of tenorite with lauryl amine as shown in Fig. 17. The reverse effect was obtained in the case of lauric acid flotation of this mineral (Fig. 18). Although it has not been proven experimentally, sulphide ions (\(\text{HS}^-\) or \(\text{S}^{2-}\)) are likely to be specifically adsorbed on oxidized copper minerals and change their electrical surface charge towards more negative values. The fact that cationic and anionic flotation of tenorite were improved and depressed, respectively, by the presence of negative sulphide ions in the pulp is in agreement with the preceding results which pointed out the importance of the mineral surface charge in ionic flotation of copper oxide.
Figure 17. Cationic flotation of tenorite with and without sulphide ions in solution (2 x 10^{-5} M lauryl amine, Procedure I).
Figure 18. Anionic flotation of tenorite with and without sulphide ions in solution. (2 x 10^{-5} M lauric acid, Procedure I).
(d) **Effect of Added Copper Ions**

Fig. 19 shows that by increasing the concentration of copper ions in solution, an inhibiting effect is observed in both cationic and anionic flotation of tenorite. Specific adsorption of hydroxo-complexes, especially larger complexes, has pronounced effects on the surface charge of some oxides (71). Perrin (112) has shown that near neutral pH's $\text{Cu}_2\text{(OH)}_2^{++}$ is the predominant copper species in solution. Copper ions were added to the flotation solutions in the expectation that larger concentrations of copper hydroxo-complexes would favour more positive values for the surface charge of tenorite and improve its floatability with anionic collector. The results obtained (Fig. 19) were opposite to those expected. However, they are consistent with the model proposed in Section 1.2.c. According to this model, $\text{H}^+$ and $\text{OH}^-$ should be the main potential-determining ions of tenorite and the concentration of copper ions in solution should not affect to any large extent the nature and magnitude of the zeta potential of the system.

The depressing action of added copper ions was observed in all the systems studied. It seems to be related to a decrease in collector concentration due to bulk interactions of the copper species (dissolved complexes or suspended colloids) with the collector. Experimental support for this proposition was obtained during the studies of adsorption of lauric acid on copper oxide substrates (to be presented in Section 4.2).

(e) **Flotation of Tenorite with Oleic Acid and Amyl Xanthate**

The results of the tests carried out using oleic acid and xanthate as collector are shown in Figs. 20 and 21, respectively. The recovery
Figure 19. Flotation of tenorite with anionic and cationic collector and in the presence of added copper ions (1 x 10^{-5} M CuSO₄) (Procedure I).
Figure 20. Flotation of tenorite with oleic acid (Procedure I).
Figure 21. Flotation of tenorite with potassium amyl xanthate (1 x 10^{-4} M solution) (Procedure I).
curves are not symmetrical about the IEP of tenorite indicating that the basic phenomena of collection cannot be accounted for by the ion adsorption theory when these collectors are used.

The optimum flotation condition as obtained from the recovery curves with oleic acid as collector, is a pH of the pulp of about 9. The recovery curves for xanthate as collector indicate that pH is not a critical variable. However, the presence of sulphide ions can be seen to increase recovery significantly. The above conditions are in agreement with plant practice for flotation of oxidized copper ores.
4.2 Infrared Spectroscopic Studies

4.2.1 Qualitative and Quantitative Analysis of the Spectra

(a) The Assignment of Bands

To facilitate the qualitative interpretation of the IR spectroscopic data obtained during the studies of adsorption of aqueous lauric acid onto copper oxide substrates (to be discussed in sub-section 4.2.2), an introductory discussion on band assignment is presented.

The following spectra are analyzed:

(i) transmission reference spectra of oxidized copper minerals;
(ii) specular reflection spectra of gold and copper oxide substrates;
(iii) ATR spectra of cuprous oxide films (alone, in the presence of H$_2$O and D$_2$O);
(iv) transmission reference spectra of carboxylic acids and soaps; and
(v) specular reflection spectra of carboxylic compounds. These include:

   (v.1) thin films of lauric and stearic acid condensed onto gold substrates from the vapour phase;
   (v.2) lauric acid adsorbed onto gold surfaces from H$_2$O and D$_2$O solutions, and
   (v.3) thin films of lauric and stearic acid condensed onto cupric oxide substrates.

(i) Transmission Reference Spectra of Oxidized Copper Minerals

The absorption spectra of cupric oxide, cuprous oxide, cupric hydroxide and malachite, which are the oxidized copper minerals most
pertinent to this work, are shown in Figs. 22 to 25. These spectra are presented in terms of absorbance versus wavenumber and they have been replotted from spectra recorded in a linear percent transmission mode. Band assignment (shown in the figures) was made on the basis of the data presented in Appendix C (table of characteristic frequencies).

(ii) Specular Reflection Spectra of Gold and Copper Oxide Substrates

In Figs. 26 (wavenumber region of 3700 to 2600 cm\(^{-1}\)) and 27 (1800 to 700 cm\(^{-1}\) region) the spectra (actual trace in 20X expanded linear transmission mode) of freshly prepared gold (curve A) and cupric oxide* (curve B) substrates are shown in order to illustrate the typical behaviour of the baselines obtained during the spectroscopic studies which were conducted using the eleven reflection, 70° incidence angle, specular reflection technique. The spectral regions represented were the most useful regions as far as the identification of surface carboxylic compounds were concerned.

All the substrates (gold or copper oxide) used in these studies showed a tendency to adsorb organic contaminants from the surroundings. This was indicated by the presence of a weak band at approximately 2900 cm\(^{-1}\) (C-H stretching vibrations of organic compounds) which increased with time of exposure of the mirrors to the atmosphere. The intensity of the CH band in the spectrum shown in Fig. 26A represents the maximum level of contamination accepted.** Mirrors for which the spectrum contained

* Spectra of cuprous oxide substrates (not shown) presented essentially the same behavior as that of cupric oxide substrates (Figs. 26 and 27 B).

** This level corresponds to less than a tenth of "complete" coverage of the mirror surface with organic species as estimated for a monolayer of stearic acid (to be shown in Part (c) of this section).
Figure 22. Absorption spectrum of cupric oxide (KBr disc).

Figure 23. Absorption spectrum of cuprous oxide (KBr disc).
Figure 26. (A) Spectrum of gold mirrors (actual trace, 3700-2600 cm\(^{-1}\) IR region).
(B) Spectrum of cupric oxide front surface gold mirrors (actual trace, 3700-2600 cm\(^{-1}\) IR region).
Figure 27. (A) Spectrum of gold mirrors (actual trace, 1800-700 cm$^{-1}$ region)
(B) Spectrum of cupric oxide covered front surface gold mirrors (actual trace, 1800-700 cm$^{-1}$ region).
a CH band more intense than that were discarded.

Copper oxide substrates yielded spectra showing a pair of very weak bands around 1500 cm\(^{-1}\) and 1400 cm\(^{-1}\) which was probably due to the presence of minor carbonate contaminants formed during exposure of the mirrors to atmospheric air containing carbon dioxide. The bands shown in Fig. 27B are typical examples. Slight differences in intensity and position were observed in carbonate bands of spectra of the various copper oxide substrates used in this research. Mrmaj\(^{113}\) also noted the presence of similar bands in reflection spectra of copper metal mirrors.

Representative reflection spectra of cuprous oxide and cupric oxide covered front surface gold mirrors are presented in Figs. 28 and 29, respectively. The assignment of the predominant band at 645 cm\(^{-1}\) in Fig. 28 to Cu\(_2\)O (or CuO\(_0.67\)) lattice vibrations, is in agreement with published data.\(^{84,85}\) A shoulder in this main band (shown at approximately 500 cm\(^{-1}\)) was observed in almost all spectra of cuprous oxide substrates. It may be associated with the presence of small concentrations of cupric oxide in those films, as suggested by their electron-diffraction pattern (see Section 3.2). The assignment of the predominant band at 570 cm\(^{-1}\) to CuO (see Fig. 29) is also consistent with previous observations.\(^{85}\) The shoulder at about 450 cm\(^{-1}\) appears to be related to the presence of cupric oxide but its real nature was not determined.

(iii) ATR Spectra of Cuprous Oxide Films

ATR spectra of thin films of cuprous oxide deposited onto KRS-5 prisms are shown in Fig. 30. When the spectrum was recorded
Figure 28. Reflection spectrum of cuprous oxide covered front surface, gold mirrors.

Figure 29. Reflection spectrum of cupric oxide covered front surface, gold mirrors.
Figure 30. ATR spectra of cuprous oxide films: (A) alone, (B) in the presence of H₂O, (C) in the presence of D₂O.
without any liquid in the reaction vessel (Fig. 30A), the Cu$_2$O band occurred at 615 cm$^{-1}$, in close agreement with values obtained by transmission spectroscopy (see Fig. 23). The shoulder to the main band, located at approximately 520 cm$^{-1}$ may be due to the presence of cupric oxide in the film as aforementioned. The presence of weak carbonate bands can also be noticed. The bands at 1200 and 1145 cm$^{-1}$ are attributed to the C-F groups of teflon. They possibly arose as a result of contact of the ATR prism with the teflon gasket used to seal the reaction vessel.

In Fig. 30, spectra B and C were taken with pure H$_2$O and D$_2$O in the reaction vessel, respectively. They illustrate the range of availability of the IR spectral region for recording of "in situ" spectra of adsorbed surface species.

(iv) Transmission Reference Spectra of Carboxylic Acids and Soaps

The IR spectra of carboxylic acids have been extensively studied and the assignment of their characteristic frequencies is well established (see Appendix C). Carboxylic acids occur as dimers in the solid or liquid state due to strong hydrogen bonding of the form

$$\begin{align*}
R-C & \quad C-R \\
\begin{array}{c}
\text{OH} \\
\end{array} & \quad \begin{array}{c}
\text{OH} \\
\end{array}
\end{align*}$$

(R = hydrocarbon radical)

The transmission spectra of lauric and stearic acid are shown in Figs. 31 and 32, respectively. These two spectra are similar in appearance with minor differences in the relative intensity of the CH$_2$ stretching
Figure 32. Absorption spectrum of stearic acid (KBr disc).

Absorbance

\[ \text{Wavenumber (cm}^{-1}) \]

- 3000
- 2500
- 2000
- 1500
- 1000
- 500
- 250

\( \nu_{\text{as CH}_2} \)
\( \nu_{\text{as CH}_3} \)
2918
2850
\( \nu_{\text{s CH}_2} \)
\( \sim 2700 \)

\( \nu_{\text{CH}_2} \text{ scissoring} \)
1698
1470
1460

\( \nu_{\text{CH}_3} \text{ scissoring} \)

\( \nu_{\text{CH}_2} \text{ rocking} \)
712

Figure 31. Absorption spectrum of lauric acid (KBr disc).

Absorbance

\[ \text{Wavenumber (cm}^{-1}) \]

- 3500
- 3000
- 2500
- 2000
- 1500
- 1000
- 500
- 250

\( \nu_{\text{OH}} \) (dimer)
\( \sim 2700 \)
2920
2955

\( \nu_{\text{C=0}} \) (dimer)
1698

\( \nu_{\text{C-OH}} \) coupled with \( \delta_{\text{OH}} \) (in-plane)
1430
1405
1305

\( \delta_{\text{OH}} \) (out-of-plane)
935
720
and bending vibration bands, and in the number and position of the bands in the region 1320 to 1170 cm\(^{-1}\) (band progression due to CH\(_2\) wagging modes). The carbonyl stretching frequency (strong band at approximately 1700 cm\(^{-1}\)) is characteristic of the dimeric structure of the acid molecules and can be used to differentiate the dimeric acids from the monomers and from the carboxylate ions (salts).

Monomers of some saturated fatty acids have been observed in dilute solutions of non-polar organic solvents or in the vapour phase. Their carbonyl stretching vibrations occur at approximately 1760 cm\(^{-1}\). Also, the monomeric species give rise to a free OH stretching band (sharp) at 3560–3500 cm\(^{-1}\) instead of the broad band of the dimers at 3000–2500 cm\(^{-1}\) (band shown at approximately 2700 cm\(^{-1}\) in Figs. 31 and 32). In addition, a pure (uncoupled) C–OH stretching band is observed at around 1375 cm\(^{-1}\) in the spectra of the monomers. The spectra of some carboxylic acids contain carbonyl bands at 1715 cm\(^{-1}\) and the single-bridge structure

...O \(\rightleftharpoons\) OH...O \(\rightleftharpoons\) OH...O \(\rightleftharpoons\) OH...

C \(\rightleftharpoons\) C \(\rightleftharpoons\) C \(\rightleftharpoons\) C
R \(\rightleftharpoons\) R \(\rightleftharpoons\) R

has been proposed.

In the case of the salts, the carboxylate ion

\[
\begin{align*}
\text{O} & \quad - \\
\text{R} - \text{C} & \quad \text{O}
\end{align*}
\]
is formed. Consequently, bands associated with the OH groups are not present in their spectra. In the spectra of sodium and cupric laurate shown in Figs. 33 and 34, the characteristic carbonyl absorption is replaced by two bands at $1610-1550 \text{ cm}^{-1}$ and $1450-1300 \text{ cm}^{-1}$ corresponding to the asymmetric and symmetric stretching vibrations of the COO$^-$ group, respectively. The carboxylate stretching bands are observed at $1555$ and $1420 \text{ cm}^{-1}$, for sodium laurate, and at $1585$ and $1433 \text{ cm}^{-1}$, for cupric laurate, in agreement with reported frequencies. The OH bands shown in the spectra (at about $3300 \text{ cm}^{-1}$) are associated with water absorbed into the potassium bromide disc and not with the carboxylic salts.

(v) Specular-Reflection Spectra of Carboxylic Compounds

(v.l) Thin films of lauric and stearic acid condensed onto gold substrates from the vapour phase.

Except for some differences in the relative intensities of bands,* the reflection spectra of thin films of lauric and stearic acid evaporated onto gold substrates (shown in Figs. 35 and 36) are very similar to the corresponding transmission spectra of these acids (Figs. 31 and 32). Acid molecules in the dimeric form seem to be the only component of the condensed films. However, treatment of the films with organic solvents removed most of the dimeric species exposing a layer of a different carboxylic structure identified from spectra.

* These differences are related to the phenomenon of molecular orientation in the films and its effect on specular reflection band intensity. This matter will be discussed in part (b) of this sub-section.
Figure 33. Absorption spectrum of sodium laurate (KBr disc).

Figure 34. Absorption spectrum of cupric laurate (KBr disc).
Figure 35. Specular reflection spectrum of lauric acid evaporated onto gold substrates.

Figure 36. Specular reflection spectrum of stearic acid evaporated onto gold substrates.
as the monomeric form of the acid. A representative spectrum of such residual films is presented in Fig. 37A. This spectrum was recorded after immersing a pair of gold mirrors bearing evaporated stearic acid films (same sample used for recording Fig. 36 spectrum) in 200 ml of carbon tetrachloride for 30 minutes and rinsing with 100 ml of the solvent. The carbonyl band characteristic of the dimer (1700 cm\(^{-1}\), in Fig. 36) was not detected in Fig. 37A spectrum but another carbonyl stretching band was exposed at around 1730 cm\(^{-1}\). This band together with a sharp band at 1380 cm\(^{-1}\) and the CH stretching vibrations in the 2900 cm\(^{-1}\) region were the only bands observed. Identification of this spectrum with that of monomeric carboxylic acid was based upon the studies of adsorption of lauric acid onto gold substrates from H\(_2\)O and D\(_2\)O solutions, which will be the subject of a later discussion (Part v.2). No attempt was made to establish the real nature of the bonds between the monomeric acid species and the gold surface.

**Strength of Adhesion of Molecules in the Condensed Films**

Several tests showed that the dimeric acid molecules (lauric or stearic acid), vapour deposited onto the gold substrates, were weakly bound to the solid surface. Spectra of films recorded after storing the mirrors in argon for a few hours showed a noticeable decrease in the intensity of the IR bands associated with the dimeric acid as compared with the spectra of the films recorded immediately after the deposition. This indicates that part of the film probably evaporated into the environment. Also, as above mentioned, short time immersion in organic solvents (hexane, carbon tetrachloride or acetone) removed most
Figure 37. Spectra of monomeric carboxylic acid formed on gold by (A) washing with carbon-tetrachloride (evaporated stearic acid films), (B) adsorption of lauric acid from H2O solutions, (C) adsorption of lauric acid from D2O solutions (spectra recorded 15 minutes after deposition).
of the dimeric species present in the condensed films. On the other hand, the residual layer seemed somewhat more adherent. A significant fraction of this layer was still detected in the spectra of mirrors treated with the organic solvents for several hours (for example, the sample used for recording Fig. 37 spectrum was subjected to a further immersion in carbon tetrachloride for 48 hours and its spectrum recorded; a $\Delta R$ value of 0.0006 for the CH$_2$ asymmetric stretching band at 2920 cm$^{-1}$ was measured and the other bands associated with the monomeric acid were still detected). The residual films were highly insoluble in water. Spectra of mirrors containing these films, recorded before and after immersion in double distilled water (500 ml) for more than 50 hours, showed no differences in band intensities or positions. It was observed that the residual layer on the gold surface increased the hydrophobic nature of the substrate. Covered gold mirrors were completely hydrophobic in contrast with the partially hydrophilic uncovered gold mirrors.

(v.2) Lauric acid adsorbed onto gold surfaces from H$_2$O and D$_2$O solutions.

The spectrum of gold mirrors exposed to a lauric acid solution ($2 \times 10^{-5}$ M lauric acid in H$_2$O, pH = 5.7, 15 minutes exposure time,* aqueous system kept under argon environment) is presented in Fig. 37B.

* Band intensities were not changed by exposing the mirrors for longer periods of time (up to 12 hours). Adhesion of the lauric acid films to the substrate was comparable to that of the carboxylic acid residual layers as estimated by solubility tests (in water and in organic solvents) analogous to those referred to in (v.1).
The presence of the carbonyl band at approximately $1730 \text{ cm}^{-1}$ and of the $1380 \text{ cm}^{-1}$ band suggested that the lauric acid film adsorbed from aqueous solution is of the same nature as the residual layer of carboxylic acid observed during the studies conducted on films formed by evaporation (compare Fig. 37A with Fig. 37B).

Effect of Deuteration on the Spectrum of the Adsorbed Film

To clarify the assignment of the bands at $1730$ and $1380 \text{ cm}^{-1}$, gold mirrors were exposed to a $\text{D}_2\text{O}$ solution of lauric acid ($2 \times 10^{-5} \text{ M}$, argon environment, 15 minutes exposure time) and the spectrum of the adsorbed deuterated acid species ($\text{C}_{11}\text{H}_{23}\text{COOD}$) was recorded (Fig. 37C). The position of the $1730 \text{ cm}^{-1}$ band was unaltered. However, the intensity of the $1380 \text{ cm}^{-1}$ band seems much reduced in comparison with the same band in Fig. 37B (hydrogenated species), indicating that the $1380 \text{ cm}^{-1}$ band is associated with a group containing OH. In this case a band associated with the corresponding deuterated group (C-OD) should have been recorded but decreased resolution in spectra recorded at lower frequencies may have obscured its identification. The presence of a weak band in the spectrum of the deuterated film at $1380 \text{ cm}^{-1}$ might be related with the fast exchange of OD by OH groups existent in the form of water vapour in the atmosphere. In fact, it was observed that the intensity of this band increased with time of exposure of the films to air; immersion of the mirrors in $\text{H}_2\text{O}$ brought the intensity of this band to the same order of magnitude of the one shown in Fig. 37B for the completely hydrogenated species.
Assignment of the 1730 cm\(^{-1}\) and 1380 cm\(^{-1}\) bands

The 1730 cm\(^{-1}\) and 1380 cm\(^{-1}\) bands were identified with the C=O and C-OH stretching modes, respectively, of monomeric acid molecules adsorbed on the gold surface.

In Chapter II it was pointed out that several investigators have reported the presence of a weak band around 1735 cm\(^{-1}\) during studies of IR spectra of adsorbed carboxylic acid species onto various substrates. They have assigned this band to the carbonyl stretching of an "ester" surface compound. Formation of a similar compound on the gold surface seems unlikely. In addition, the "ester" hypothesis would not explain the presence of the relatively strong band at 1380 cm\(^{-1}\). Eischens,\(^9\) working with acetic acid attributed a band at 1389 cm\(^{-1}\) to CH\(_3\) bending vibrations of the surface "ester". A similar assignment to the 1380 cm\(^{-1}\) band of the spectra of films adsorbed on gold (Figs. 37A and 37B) can be ruled out in view of the results of the experiments conducted using D\(_2\)O solutions of lauric acid which indicated that this band is associated with a hydroxylated group. The fact that C=O and C-OH bands have been reported at 1735 cm\(^{-1}\)\(^{114}\) and 1375 cm\(^{-1}\)\(^{117}\) (see Appendix C), respectively, further supports the proposed assignments.

(v.3) Thin films of lauric and stearic acid condensed onto cupric oxide substrates.

Lauric and stearic acid films deposited from the vapour phase onto cupric oxide substrates yielded spectra similar to those recorded for films condensed on gold surfaces (Figs. 35 and 36) indicating that the dimeric form of the acids is the major component of these films.
However, a band at 1583 cm$^{-1}$, very weak in spectra recorded immediately after deposition but increasing with time, was observed in the case of cupric oxide substrates. This is illustrated in Figs. 38 and 39 which show the spectra of stearic acid films evaporated onto cupric oxide substrates and recorded 30 minutes and 90 hours after the deposition, respectively.

The 1585 cm$^{-1}$ band was assigned to the asymmetric stretching of cupric carboxylate (see transmission spectrum of cupric laurate given in Fig. 34) formed by reaction of the acid molecules with cupric oxide. This band increases in intensity as the carbonyl stretching of the dimeric acid (1700 cm$^{-1}$) decreases. The symmetric stretching of the carboxylate ions (expected at 1433 cm$^{-1}$) was not observed probably because of superposition of the 1430 and 1410 cm$^{-1}$ bands of the acid (C-OH stretching coupled with in-plane OH bendings). A noticeable decrease in intensity of the CH$_2$ stretching bands (2900 cm$^{-1}$ region) with longer reaction times indicated that the carboxylic species were loosely bound in the film. Washing the mirrors with organic solvents exposed a residual layer of carboxylic surface compounds.

A representative spectrum of the residual layer is shown in Fig. 40. This spectrum was recorded after immersion of the sample, used for recording the spectrum of Fig. 39 in carbon tetrachloride (200 ml) for 30 minutes and rinsing with 100 ml of the solvent. It is apparent from the spectrum that virtually all cupric stearate and dimeric acid molecules have been removed by the solvent. The low concentration of the residual adsorbate and the fact that carbonate bands are possibly underlying the bands associated with the carboxylic species in the region 1500 to 1400 cm$^{-1}$ (see spectrum of the substrate alone; Fig. 27)
Figure 38. Specular reflection spectrum of stearic acid deposited on cupric oxide substrates from the vapour phase (recorded 30 minutes after deposition).

Figure 39. Specular reflection spectrum of stearic acid evaporated onto cupric oxide substrates (90 hours after deposition).
Figure 40. Spectrum of stearic acid film deposited by evaporation onto cupric oxide substrate (residual layer observed after treatment of mirrors with carbon tetrachloride).

Figure 41. Difference spectrum of the residual layer (spectrum of Fig. 40 minus spectrum of unreacted cupric oxide substrate).
make the assignment of bands of the spectrum of the remaining species rather difficult. However, the difference spectrum* of the film (Fig. 41) indicated that the residual layer is composed of two different carboxylic compounds. One compound yielding a carbonyl band at approximately 1730 cm\(^{-1}\) is probably the monomeric acid hydrogen bonded to the oxidized copper surface. The assignment of the 1730 cm\(^{-1}\) band to the carbonyl stretching of the monomer was discussed in the preceding part of this section (v.2) and the proposition that the molecules were hydrogen bonded to the surface seems reasonable in view of the composition of the cupric oxide surface (mainly polar groups containing oxygen and hydrogen atoms). The C-OH stretching band which appeared at 1380 cm\(^{-1}\) in the spectrum of monomeric acid attached to the gold surface is not clearly discernable in Fig. 41 spectrum. This is probably due to the presence of stronger bands around 1400 cm\(^{-1}\) to 1450 cm\(^{-1}\). Another possibility is that hydrogen bonding between C-OH groups of the monomeric acid molecules and the oxidized copper surface might have shifted this stretching band from 1380 cm\(^{-1}\) (position for the free group) to a higher wavenumber (1400-1500 cm\(^{-1}\)).

The carbonyl stretching of a second surface compound is shown at approximately 1530 cm\(^{-1}\) in Fig. 41. This frequency is more characteristic of an ionic carboxylate compound (see Appendix C) suggesting that electrostatic forces are involved in the process of adsorption of this second compound. Better quality spectra of analogous carboxylate

* The difference spectrum is obtained by subtracting the spectrum of the unreacted substrate from the spectrum of the mirrors covered with the adsorbate. Difference spectra are useful for qualitative analysis only.
species were observed during the studies of deposition of monolayers onto cupric oxide substrates from the air-water interface. They will be discussed in Part (c) of this section together with quantitative aspects of the specular reflection spectra.

(b) Effects of Molecular Orientation on IR Specular Reflection Spectra

Monolayer Transferred from the Air-Water Interface onto Smooth Gold Substrates

The most striking effects of molecular orientation were observed during the specular reflection spectroscopic studies conducted on stearic acid monolayers which had been deposited as single layers on smooth gold surfaces according to the Langmuir-Blodgett method. The spectrum of one of these monolayers, recorded 10 minutes after the deposition, is shown in Fig. 42. The spectrum of the same monolayer recorded 24 hours later (mirrors stored in argon) is presented in Fig. 43 showing a substantial increase in the intensity of bands. The intensity (ΔR) of the CH$_2$ asymmetric stretching band (2920 cm$^{-1}$) is 15 times greater in Fig. 43 than in Fig. 42. The experiment has been repeated several times; as the lapse of time between the deposition and the recording of the spectra increased the reflection bands also increased. The rate of increase of intensity of the bands varied quite considerably between experiments, but, in all of them, band intensities showed a maximum value (ΔR = 0.017 ± 0.002) for the CH$_2$ asymmetric vibration band.

This behavior might be explained by the Francis and Ellison theory (Chapter II) if the following assumptions are made:
Figure 42. Spectrum of a monolayer of stearic acid deposited onto smooth surface, gold mirrors (spectrum recorded 10 minutes after deposition).

Figure 43. Spectrum of a monolayer of stearic acid deposited onto smooth surface, gold mirrors (recorded 24 hours after deposition).
(1) The monlayers were transferred from the trough to the gold as "hydrous layers",* and with the acid molecules oriented with the hydrocarbon chains in a position nearly normal to the surface as illustrated schematically below. The dipole moment changes of the CH$_2$

![Diagram](Hydrocarbon Chain, Intervening Water Layer, Solid)

vibration modes were oriented preferentially parallel to the surface, in the most unfavourable position for interaction with the component of the radiation parallel to the plane of incidence (only component capable of interaction). As a consequence, the CH$_2$ stretching bands appeared extremely weak in Fig. 42 (compare relative intensity of bands in this spectrum with that in spectrum of Fig. 32). The presence of an intervening water layer is indicated by the (weak) bands at approximately 3300 and 1600 cm$^{-1}$ in the spectra of the monolayers. Another support for the assumption mentioned above is the presence of the carbonyl band at 1710 cm$^{-1}$ in Fig. 42. This frequency is closer to that reported for the carbonyl stretching of single-bridge acid molecules (1715 cm$^{-1}$) than those of the dimer (1700 cm$^{-1}$) or the monomer attached to the gold surface (1730 cm$^{-1}$) observed in this work. This then suggests that

* Hydrous layer is the denomination given by Langmuir for monolayers deposited with a water layer between them and the substrate (usually a non-reactive substrate).
the molecules are arranged in the transferred films in a way analogous to their disposition at the air-water interface. In other words, the single hydrogen bonds between the carbonyl groups of the fatty acid molecules formed in solidified monolayers of the acid, as proposed by previous investigators,\textsuperscript{119} are preserved in the transferred layers.

(ii). As the intervening water layer evaporates, a subsequent rearrangement of the molecules occurs. Dimeric acid molecules are formed and grouped together in crystallites with their hydrocarbon chains lying preferentially parallel to the surface. This $90^\circ$ rotation of the molecular axis brings the predominant direction of the dipole moment change of the CH\textsubscript{2} vibration modes from the most unfavourable position for interaction with the parallel component of the radiation, to the most favourable (dipole moment changes nearly normal to the surface). Consequently, an enormous increase in the intensity of the CH\textsubscript{2} stretching bands of spectra recorded after allowing time for evaporation of the intervening water layer (Fig. 43) was observed. The fact that water bands present in the spectra recorded immediately after deposition (Fig. 42) were not observed in spectra recorded at a later stage (Fig. 43) is in agreement with the hypothesis that the intervening water layer evaporates. Also, the carbonyl stretching band present at 1710 cm\textsuperscript{-1} in Fig. 42 was shifted to a slightly lower frequency (1700 cm\textsuperscript{-1}) in Fig. 43 giving support for the replacement of the single-bridge structure by dimeric acid species. "Overturning" of molecules and formation of crystallites (spots or striations) in monolayers deposited onto non-reactive substrates have been reported in the literature.\textsuperscript{118,120}
Estimation of \( \Delta R \) Values on the Basis of the Francis and Ellison Theory

A \( \Delta R \) value of 0.0079 was calculated using Francis and Ellison's equation [8] (Chapter II) for the CH\(_2\) asymmetric stretching band (2920 cm\(^{-1}\)) in a hypothetical reflection spectrum of a monolayer composed of randomly oriented stearic acid molecules (see calculation in Appendix G). The \( \Delta R \) maximum \( 0.017 \pm 0.002 \) measured for the CH\(_2\) asymmetric stretching band in the spectrum of stearic acid monolayers deposited onto smooth gold substrates (hydrocarbon chain of the acid molecules oriented preferentially parallel to the surface) is approximately 2.15 times greater than that calculated for the case of an isotropic film \( (r = \Delta R_{\text{vas,CH}_2}/\Delta R_{\text{vas,CH}_2 \text{ random}} = 2.15) \).

If effects of anisotropy on the probability that a molecule (or group) will undergo a transition are taken into account, a ratio \( r = \Delta R_{\text{vas,CH}_2 \perp} / \Delta R_{\text{vas,CH}_2 \text{ random}} = 2.46 \) might be expected (see Appendix H). This value of \( r \) is in close agreement with that obtained by using the value of \( \Delta R_{\text{as,CH}_2 \perp} \) measured from the spectrum of the stearic acid monolayer. This supports the correlation drawn between the predictions of the Francis and Ellison theory and the interpretations of these spectroscopic studies.

Monolayer Transferred to Rough Gold Substrates

Further support for the Francis and Ellison theory was obtained from the analysis of spectra of stearic acid monolayers (single layer)

* This is so in view of the spectrophotometric error in measuring \( \Delta R \) (+10%) and the approximations involved in the calculation of \( \Delta R_{\text{vas,CH}_2 \text{ random}} \) for the hypothetical monolayer (Appendix G).
deposited onto rough gold mirrors (the degree of roughness of these mirrors is illustrated in Fig. 11; compare the topography of the surface of these mirrors with that of smooth gold substrate shown in Fig. 10). The intensity of the CH\textsubscript{2} stretching bands of the spectra approached that calculated for a hypothetical randomly oriented monolayer (Appendix G).

Spectra of monolayers deposited on rough gold are shown in Figs. 44 (recorded 10 minutes after deposition) and 45 (24 hours later). Similar to the case of stearic acid monolayers deposited on smooth gold surfaces, discussed above, band intensities increased with the interval of time between the recording of the spectra and the deposition of the monolayer. This indicates that single-bridge molecules lying with their hydrocarbon chains approximately normal to the surface were converted to dimeric species, as the intervening water layer was evaporated. However, in the case of rough substrates, the maximum ΔR value for the CH\textsubscript{2} asymmetric stretching band was substantially lower (Fig. 45) than that observed for the case of smooth substrates (Fig. 43). The measured maximum ΔR\textsubscript{vas,CH\textsubscript{2}} value of 0.0065 ± 0.0010 is close to that calculated for the hypothetical isotropic monolayer (0.0079), suggesting that the dimeric acid molecules are disposed with their hydrocarbon chains following the rough contour of the substrate.

Films deposited from the Vapour Phase

Comparison between specular reflection spectra of carboxylic acid molecules condensed onto gold or copper oxide substrates (Figs. 35, 36, and 38) and the corresponding transmission spectra (Figs. 31 and 32)
Figure 44. Spectrum of a monolayer of stearic acid deposited onto rough surface, gold mirrors (recorded 10 minutes after deposition).

Figure 45. Spectrum of a monolayer of stearic acid deposited onto rough surface, gold mirrors (recorded 24 hours after deposition).
showed remarkable differences in relative band intensities which can be explained by assuming that the evaporated films have anisotropic optical properties.

The most obvious difference (see for example Fig. 36 spectrum) is the much higher intensity of the CH asymmetric stretching band in relation to any other band of the spectrum. The CH vibrations (e.g., 2960 cm\(^{-1}\) band), the carbonyl stretching (1700 cm\(^{-1}\) band) and the bands associated with coupling of C=O stretching and OH in-plane deformation modes (1430, 1410, and 1300 cm\(^{-1}\)) are weaker in comparison to the CH asymmetric stretching band (2920 cm\(^{-1}\)) but not in comparison with the other bands of the spectrum. The OH stretching of the dimer (3000-2500 cm\(^{-1}\) region, in the absorption spectra) and the out-of-plane bending of pure OH groups (approximately 935 cm\(^{-1}\)) are practically nonexistent in the reflection spectra. Also, the bands related with CH symmetric stretching (2850 cm\(^{-1}\)) and bending vibrations (scissoring at 2470 cm\(^{-1}\)) appear abnormally weak in the reflection spectra.

The above differences in relative band intensities can be explained on the basis of the Francis and Ellison theory if it is assumed that molecules in the evaporated films were condensed with their hydrocarbon chains oriented preferentially parallel to the surface. In addition, it is necessary to assume further that the hydrogen atoms of the CH\(_2\) groups are disposed nearly normal to the surface and the ring-like structure formed by the hydrogen bonded dimeric carbonyl groups lies in planes approximately normal to the surface (see model illustrating the proposed orientation of the molecules in Fig. 46). For acid molecules oriented in this way, the direction of the dipole moment change produced
Figure 46. Orientation of stearic acid molecules (dimeric) in films deposited from the vapour phase.
by the CH$_2$ asymmetric stretching mode,

\[
\begin{array}{c}
\text{C} \\
\text{H} \\
\end{array}
\]

is nearly normal to the surface (most favourable position for interaction with the "active" parallel component of the radiation), explaining the abnormally strong 2920 cm$^{-1}$ band in the reflection spectra. On the other hand, the CH$_2$ symmetric stretching,

\[
\begin{array}{c}
\text{C} \\
\text{H} \\
\end{array}
\]

the CH$_2$ scissoring,

\[
\begin{array}{c}
\text{C} \\
\text{H} \\
\end{array}
\]

the OH stretching and the OH out-of-plane bending,

\[
\begin{array}{c}
\text{O} \\
R-C \\
\end{array}
\]

produce dipole moment changes nearly parallel to the reflecting surface (most unfavourable position), yielding extremely low intensity bands at 2850, 1470, 3000-2500, and 935 cm$^{-1}$, respectively. Also, according to the model shown in Fig. 46, dipole moment changes associated with in-plane OH deformation modes,
are oriented preferentially normal to the surface and the intensity of the reflection bands arising from their coupling with the C-OH stretching vibrations (1430, 1410, and 1300 cm\(^{-1}\)) might be expected to be slightly enhanced. The direction of the dipole moment changes of other vibration modes such as CH\(_3\) vibrations, C=O and C-OH stretching vibrations should not be strongly affected by orientation of the molecules.

(c) **Langmuir-Blodgett Monolayers of Stearic Acid Deposited onto Cupric Oxide Substrates**

**Composition of the First Layer**

A representative spectrum of a monolayer of stearic acid transferred from the Langmuir trough to cupric oxide coated front surface gold mirrors is shown in Fig. 47 (actual trace, 3700-2600 cm\(^{-1}\) region) and Fig. 48 (1800-700 cm\(^{-1}\), difference spectrum also shown). The sensitivity of the multiple specular reflection technique to record spectra of surface films at surface concentration levels of monolayer coverage is illustrated. These spectroscopic results indicated that the major component of the first layer transferred from the air-water interface to cupric oxide substrates is an ionic carboxylate surface compound. Some monomeric acid molecules are also present in the film, but no evidence for the formation of cupric stearate or dimeric acid molecules was observed.
Figure 47. Spectrum of a monolayer of stearic acid deposited on cupric oxide substrate (actual trace, 3700-2600 cm\(^{-1}\) region).
Figure 48. Spectrum of a monolayer of stearic acid deposited on cupric oxide substrate: (A) Actual trace (1800-700 cm⁻¹ region), (B) Difference spectrum.
The bands at approximately 1530 and 1400 cm\(^{-1}\) in Fig. 48 were assigned to the asymmetric and symmetric stretching vibrations of the stearate ion adsorbed at the surface. A weak band at around 1730 cm\(^{-1}\) suggested the presence of the monomeric acid. The other bands shown in the spectrum of the monolayer (Figs. 47 and 48) are associated with stretching or bending vibrations of CH\(_2\) and CH\(_3\) groups. The characteristic bands of the dimeric acid (1700 cm\(^{-1}\)) or the cupric stearate (1585 cm\(^{-1}\)) were not observed.

Composition of the Subsequent Layers

Fourteen additional monolayers were transferred from the air-water interface to cupric oxide substrate covered with the first layer (total of 15 layers). Spectra of the subsequent layers (odd number layers only) were recorded. Dimeric stearic acid and cupric stearate were analyzed as the components of the subsequent layers. The spectra of 3 and 9 layers are shown, as examples, in Figs. 49 and 50, respectively. Spectrum B in Fig. 49 represents the different spectrum of the 2nd and 3rd monolayers (spectrum of 3 layers minus spectrum of the first monolayer). The identification of stearic acid (dimer) and cupric stearate as the only components of the subsequent layers is apparent from the comparison of Figs. 49 and 50 with the absorption spectra of carboxylic compounds given in Part (a) of this section.

Some Properties of the Langmuir-Blodgett Monolayers

Films formed by depositing successive monolayers of stearic acid onto cupric oxide substrates from the Langmuir trough were more stable than those condensed onto the mirrors from the vapour phase. As
Figure 49. (A) Spectrum of 3 layers of stearic acid deposited on cupric oxide substrates.
(B) Difference spectrum of 2nd and 3rd layers.

Figure 50. Spectrum of 9 layers of stearic acid deposited on cupric oxide substrate.
discussed in Part (a), evaporated films of stearic acid showed a tendency to escape into the atmosphere and also to react with the oxidized copper substrate to form cupric stearate. Spectrum of 15 monolayers (not shown) recorded after storage of the mirrors in argon for several days presented no detectable difference in band intensity or position as compared with the spectrum of the same film of 15 layers recorded immediately (10 minutes) after the deposition. The fact that no reaction between the acid molecules and the substrate was observed in this experiment suggested that the cupric stearate present in the subsequent layers was formed inside the trough, probably by the interaction of dissolved copper species with the solidified monolayers. In fact, a decrease in thickness of the cupric oxide substrate of the order of 50 Å was noticed after immersing the mirrors in the trough solution (30 minutes) at pH 4.5 for deposition of the first layer. Immersion of the substrate in the trough for deposition of the subsequent layers produced further dissolution but, in this case, at a much slower rate; only 30 Å decrease in thickness after 7 immersions required for deposition of the 14 subsequent layers.

Treatment of the Langmuir-Blodgett films with organic solvents promoted fast removal of the subsequent layers but failed to affect the first monolayer, supporting the view that the ionic carboxylate species (and the monomeric acid molecules) were chemisorbed onto the cupric oxide substrate. Spectra of mirrors covered with a monolayer of stearic

* Changes in cupric oxide film thickness were calculated from measured AR values at band maximum (570 cm\(^{-1}\)) and by means of equation I\(_2\) given in Appendix I.
acid measured after immersion in carbon tetrachloride, hexane or acetone (up to 48 hours) yielded identical bands to those shown in Figs. 47 and 48 (untreated monolayer). Other mirrors were immersed in pure water for several days and again no change in the composition of the adsorbed monolayer was observed. The presence of the monolayer on the mirrors changed the hydrophilic nature of the cupric oxide surface to hydrophobic.

The high stability of the Langmuir-Blodgett films can be understood by considering that molecules in the solidified monolayers were in a close-packed arrangement and consequently strong van der Waals attractions between hydrocarbon chains were developed.

**Band Intensity**

Spectra of stearic acid monolayers transferred from the air-water interface to cupric oxide substrates were recorded with the objective of establishing standard references for quantitative analysis of similar carboxylic films. However, the following points must be observed:

(i) More than one carboxylic compound was present in the deposited monolayers which made impossible the determination of their actual concentrations from the trough data. Therefore, bands associated with vibration modes of carbonyl groups are not useful for quantitative purposes.

(ii) The transferred films presented anisotropic optical properties due to preferential orientation of the molecules. The concentration of CH$_2$ groups in the monolayers can be estimated from the trough data but
effects of molecular orientation on the specular reflection spectra (discussed in Part (b)) should be taken into account before using the intensities of the CH$_2$ bands as quantitative references.

ΔR values for the CH$_2$ asymmetric stretching band (2920 cm$^{-1}$) were measured from the spectra of the transferred monolayers and plotted against the number of layers in Fig. 51. Point P1 (one monolayer) represents the average of a series of measurements made using five different samples prepared under similar conditions. The ΔR values for the CH$_2$ asymmetric stretching band of the spectra of these first monolayers were measured as 0.0025 ± 0.0001.

According to the Francis and Ellison theory, a linear plot of ΔR of the CH$_2$ asymmetric stretching band versus film thickness (or number of layers) should be expected if the hydrocarbon chain of the molecules were identically oriented in each layer. The concentration of CH$_2$ groups was the same for any layer (same transfer ratio, 1 ± 0.02), therefore suggesting that the non-linearity observed in Fig. 51 plot might be related to differences in orientation of molecules in the various layers.

**Effects of Molecular Orientation on the Spectra of Monolayers Deposited on Cupric Oxide Substrates**

The behavior of the curve obtained by plotting ΔR (CH$_2$ asymmetric stretching) versus number of layers of stearic acid transferred from the trough to cupric oxide substrates (Fig. 51) might be explained by differences in molecular orientation in the various layers. The observed deviation from linearity in the curve shown in Fig. 51 is manifested in two ways:
Figure 51. Measured $\Delta R$ values for the $\text{CH}_2$ asymmetric stretching band (2920 cm$^{-1}$) of spectra of stearic acid monolayers transferred to cupric oxide substrates.
1. The intensity of the CH$_2$ stretching band of the spectra of the first layer is somewhat higher than the average intensity per layer of the corresponding band in spectra of subsequent layers. This might be due to the fact that CH$_2$ groups of subsequent layers are oriented in planes nearly parallel to the reflecting surface and the molecules in the first layer are more randomly oriented. In this case, the chemisorbed molecules of the first layer are disposed with their hydrocarbon chains sticking out of the cupric oxide substrate but following the relatively rough surface contour. Dissolution of the film inside the trough is responsible for an increase in roughness of the substrate. This was verified by interferometric and electron-microscopic studies conducted on cupric oxide surfaces which have been exposed to chemical environments similar to those which exist in the trough. The increase in the degree of roughness of cupric oxide surfaces resulting from immersion in H$_2$SO$_4$ solution (pH 4.5) for 30 minutes (same conditions used during actual deposition of a monolayer) is illustrated in Fig. 52.

2. The contribution of individual layers to the intensity of the CH$_2$ asymmetric stretching band of spectra of multilayers increases with the number of layers (increasing slope in Fig. 51 curve). This phenomenon can be attributed to a partial degradation of molecular orientation in the thicker films or (and) an increase in the angle formed by the planes containing oriented CH$_2$ groups with the reflecting surface.

Takenaka and co-workers$^{121}$ used a polarized infrared ATR technique for calculating the angle formed by the plane of CH$_2$ groups with the
52(a) Fizeau interference fringes (fringe-to-fringe spacing = 2945 Å, 15 x horizontal magnification).

52(b) Transmission electron micrograph (acetate replica)

Figure 52. Surface topography of cupric oxide substrates exposed to $10^{-4.5}$ M $\text{H}_2\text{SO}_4$ solution for 30 minutes.
solid surface in built-up films of stearic acid (up to 201 layers) deposited onto a germanium prism. Their results showed angles (average) varying from 27-30° for thinner films (e.g., 9 and 11 layers) to 35° for thicker films. They considered the angle formed by the molecular axis with the plane normal to the surface in the case of thin films (29-30°) to be close to the crystallographic angle between the C- and C'- axes of the stearic acid crystal (26.4°). They explained the increase in this angle with increase in the number of layers by degradation of molecular orientation in the thicker films.

Table 4 shows values for the average angles formed by planes containing CH2 groups with the solid surface (first layer not included) as estimated using ΔR values from Fig. 51 and applying the Francis and Ellison theory. (see detail of calculation in Appendix J). The calculated angles varied from 15.4 to 17.4.* These angles were significantly lower than the corresponding angles reported by Takenaka and associates mentioned above. The discrepancy might be due to the lower surface pressure (16.5 dynes.cm\(^{-1}\)) used by them during transfer of the monolayers, as compared to the pressure of 27 ± 1 dynes.cm\(^{-1}\) employed in this work.

* These angles are closer to the angle (minus 90°) made by the carbon tetrahedral bonds with the axis of the hydrocarbon chain (109° 28' - 90° = 19° 28') (ref. 122) than to the crystallographic angle of the stearic acid crystal (26.4°).
Table 4. Average angle made by planes containing CH₂ groups of stearic acid molecules in the subsequent layers with the solid surface.

<table>
<thead>
<tr>
<th>Number of layers (m)</th>
<th>ΔR</th>
<th>ΔRₐₙ-ΔR₁ₘ</th>
<th>Average ΔR  ( \frac{ΔRₐₙ-ΔR₁ₘ}{m-l} )</th>
<th>Average * angle ( \theta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>.0025</td>
<td>-</td>
<td>(.0025)</td>
<td>(21°)</td>
</tr>
<tr>
<td>3</td>
<td>.0053</td>
<td>.0028</td>
<td>.00140</td>
<td>15.6°</td>
</tr>
<tr>
<td>5</td>
<td>.0081</td>
<td>.0056</td>
<td>.00140</td>
<td>15.6°</td>
</tr>
<tr>
<td>7</td>
<td>.0107</td>
<td>.0082</td>
<td>.00137</td>
<td>15.4°</td>
</tr>
<tr>
<td>9</td>
<td>.0141</td>
<td>.0116</td>
<td>.00145</td>
<td>15.8°</td>
</tr>
<tr>
<td>11</td>
<td>.0174</td>
<td>.0149</td>
<td>.00149</td>
<td>16.0°</td>
</tr>
<tr>
<td>13</td>
<td>.0223</td>
<td>.0198</td>
<td>.00165</td>
<td>16.9°</td>
</tr>
<tr>
<td>15</td>
<td>.0267</td>
<td>.0242</td>
<td>.00174</td>
<td>17.4°</td>
</tr>
</tbody>
</table>

* Detail of calculation given in Appendix J.
4.2.2 Adsorption of Aqueous Lauric Acid onto Copper Oxide Substrates

(I) Specular Reflection Spectroscopic Studies

In agreement with the results of the flotation tests discussed in Section 4.1, adsorption experiments conducted using the specular reflection spectroscopic technique showed that mineral surface charge was the major variable affecting adsorption of aqueous lauric acid onto cupric oxide substrate. The relationship between adsorption of collector, surface charge and floatability was in this way established. Chemisorption of laurate ions as counter ions in the internal part of the double layer (mechanism B.ii.c, Table 1) was postulated as the predominant adsorption mechanism leading to collection. Co-adsorption of monomeric lauric acid molecules was observed as a secondary phenomenon. It was suggested that the neutral acid molecules were attached to the solid surface by means of strong hydrogen bonding (mechanism A.iii, Table 1).

Experiments carried out using cuprous oxide substrate yielded results analogous to those obtained with cupric oxide. Variables such as added copper ions, surfactant concentration, time of exposure, partial pressure of carbon dioxide, the presence of oxygen in the system and agitation of the aqueous medium were investigated and their roles in the adsorption process were found to be insignificant in comparison with the effects of pH.

(a) Effects of pH on Adsorption of Lauric Acid onto Cupric Oxide Substrate

The effect of pH on adsorption of aqueous lauric acid onto cupric
oxide covered front surface gold mirrors was investigated by recording IR spectra of mirrors before and after their exposure to lauric acid solutions which contained no added copper ions and were kept under a controlled argon atmosphere. ΔR values for the CH₅ asymmetric stretching band of spectra of adsorbates measured during tests conducted using 2 x 10⁻⁵ M lauric acid solutions (same collector concentration employed during flotation tests), are plotted against pH ranging from 4.7 to 10.5 in Fig. 53. The mirrors were immersed into the solution for 5 minutes (time equivalent to that used for conditioning the flotation samples) and the solution was not stirred during the exposure. Typical behavior of the adsorbate spectra are shown in Fig. 54 (spectrum A, solution at pH 4.7; spectrum B, pH 8.4; and spectrum C, pH 10.5).

Correlation between Adsorption and Flotation

The close correlation between mineral floatability and adsorption of lauric acid onto cupric oxide substrate is apparent from the comparison of the adsorption curve (Fig. 53) with the flotation curve (Fig. 16). This indicates that mineral surface charge is the major factor governing adsorption of the anionic surfactant.

Fig. 53 shows that cupric oxide does not adsorb lauric acid from solutions at pH's above the IEP (approximately pH 9.4). Also, visual inspection of the mirrors indicated that their surface remained hydrophilic after the exposure to these solutions.

As the pH of the solution was lowered to values below the IEP, and consequently as the positive surface charge increased, adsorption also
Figure 53. Adsorption of aqueous lauric acid (2 x 10^{-5} M) onto cupric oxide substrate (system under argon atmosphere, no copper ions added, no agitation of the solution, 15 minutes reaction time).
Figure 54. Reflection spectra of cupric oxide substrates exposed to aqueous lauric acid (2 x 10^{-5} M, system under argon atmosphere, no added copper ions, no agitation, 15 minutes exposure time). (A) pH 4.7; (B) pH 8.4; (C) pH 10.5
increased up to a maximum at approximately pH 7.5. Below this pH no further change in the adsorbate concentration was observed. The surface of the mirrors treated with solutions at pH's between 9.5 and 7.5 had partially hydrophobic properties. Complete hydrophobicity of the surface was only observed for mirrors exposed to solutions at pH's below 7.5.

**Monolayer Coverage**

The expected $\Delta R$ value for the CH$_2$ asymmetric stretching band of the spectrum of a monolayer formed by adsorption of lauric acid onto cupric oxide can be estimated, from spectroscopic data obtained in sub-section 4.2.1, as $0.00156 \pm 0.0001$. Since in the region of maximum adsorption (Fig. 53) the observed $\Delta R$ has values $0.0015 \pm 0.0001$, it can be assumed that "complete" surface coverage by a monolayer occurred when the substrate was treated in solutions at pH's corresponding to those of best floatability of tenorite (pH's below 7.5).

**Composition of the Surface Films**

Representative spectra of samples exposed to solutions at pH's characteristic of the three different adsorption regions, i.e. region of "complete" surface coverage, region of partial coverage, and, no adsorption region, are shown in Fig. 54 (spectrum A, B, and C, respectively). Laurate ions and monomeric lauric acid were identified as the components of the adsorbed films.

*In sub-section 4.2.1 it was shown that $\Delta R_{\text{vas,CH}_2}$ for the spectra of stearic acid monolayers (16 CH$_2$ groups) deposited as single layers on cupric oxide was $0.0025 \pm 0.0001$. For a monolayer of lauric acid (10 CH$_2$ groups), assuming that the CH$_2$ groups are oriented similarly to those of the stearic acid molecules: $\Delta R = (0.0025 \pm 0.0001) \times 10/16 = 0.00156 \pm 0.00001$.}*
Spectrum A resembles that of a single monolayer of stearic acid deposited onto cupric oxide substrate by the Langmuir-Blodgett method (compare difference spectra of Fig. 54A with that of Fig. 48). Bands at approximately 1530 and 1400 cm$^{-1}$ were assigned to the asymmetric and symmetric stretching of the carbonyl group (COO$^-$) of the adsorbed laurate ions. The presence of a weaker carbonyl band at 1730 cm$^{-1}$ suggests that monomeric acid molecules were also adsorbed.

Spectra of films formed at pH's between 7.5 and 9.5 (spectrum B, Fig. 54) show carbonyl bands for the ionic species and the monomer acid of the same order of magnitude. Fig. 54, spectrum C, illustrates the fact that organic species were not adsorbed from solutions at pH's greater than 9.5.

Adhesion of the Adsorbed Species

Tests carried out with the purpose of investigating the strength of adhesion of the adsorbed carboxylic film indicated that strong chemical forces were developed between the adsorbate and the cupric oxide substrate. Spectra of adsorbed films (total or partial surface coverage) recorded before and after storing the mirrors in argon, or immersing them in pure double distilled water (pH 6.7)*, for periods of time up to 100 hours showed no noticeable difference in intensity or position of bands. Furthermore, the films were also resistant to organic solvents: immersion (up to 12 hours) in the solvents employed in this work failed to produce any significant difference in the spectra. Immersion of the mirrors in water at pH's greater than approximately 9.5 removed the adsorbed film.
of the adsorbed films (except for a small decrease in the intensity of the 1730 cm$^{-1}$ band during prolonged exposure to a strong polar solvent such as acetone).

Support for the Mechanisms of Adsorption

The hypothesis that ionic laurate species were chemisorbed as counter ions in the internal part of the double layer is supported by:

(i) the established correlation between adsorption and substrate surface charge;

(ii) the presence of COO$^-$ carbonyl bands in the spectra of the adsorbed films;

(iii) the fact that adsorption did not exceed "complete" surface coverage; and,

(iv) the strong adhesion of the adsorbate to the substrate.

Chemisorption of neutral acid species is supported by:

(i) identification of the 1730 cm$^{-1}$ band of the spectra of the adsorbed films with the carbonyl band associated with monomeric acid molecules probably hydrogen bonded to the substrate (see Section 4.2.1(a)),

(ii) the strong nature of the adhesion, and

(iii) the "sub-monolayer" coverage of the surface.

In general, adsorption of neutral species is not affected by the substrate surface charge. Lack of adsorption of monomeric acid species onto cupric oxide from solutions at pH's above 9.5 might be due to depletion of neutral acid molecules in the bulk by dissociation at more basic pH's (see ionization constant, Appendix A).
(b) **Effect of Time of Exposure and Agitation**

Further support for the proposed adsorption mechanisms was obtained from the results of adsorption tests carried out using longer exposure times and/or stirring the solution (other conditions were identical to those of the experiments reported in Part (a)).

Mirrors exposed to solutions at pH's lower than 7.5 for longer periods of time (up to 10 hours) showed no detectable increase in the amount of carboxylic species adsorbed (measured from $\Delta R_{\text{vas}, \text{CH}_2}$ of the spectra) beyond that observed in experiments discussed in Part (a)). This observation is consistent with the hypothesis of formation of a "complete" monolayer by chemisorption. Films adsorbed from solutions at pH's in the 7.5 to 9.5 range, showed an increase in $\Delta R_{\text{vas}, \text{CH}_2}$ of spectra recorded after longer exposure time, but adsorption never exceeded the calculated value for a "complete" monolayer in agreement with the proposed chemical nature (strong hydrogen bonding) of the adsorption of the monomeric acid molecules. A corresponding increase in the 1730 cm$^{-1}$ monomeric acid band was also noticed in this case. Such increase supports the explanation given in Part (a) for the decrease in adsorption of the neutral species at more basic pH's (dissociation of the acid, depletion of neutral species in the bulk). At no time did adsorption occur in samples treated with solutions at pH's above 9.5.

Tests carried out with the solution being stirred yielded spectra of adsorbed films similar to those obtained with stagnant solutions indicating that agitation was ineffective in promoting adsorption or desorption of the chemisorbed organic films. However, stirring
affected the rate of dissolution of the substrate slightly. For example, in the absence of agitation, no dissolution of the cupric oxide film was detected in tests conducted under basic pH conditions; mirrors immersed in solutions at pH 5.5 for 10 hours resulted in a decrease in film thickness of approximately 30 Å (measured from the decrease in ΔR values of the CuO band at 570 cm⁻¹). When mirrors were exposed to agitated solutions, dissolution was observed in basic media (a 20 Å decrease in thickness of films treated at pH 10.5 for 10 hours); mirrors immersed in pH 5.5 solutions (10 hours) showed a decrease in film thickness of approximately 60 Å.

(c) **Effect of Surfactant Concentration**

Experiments similar to those described in Part (a) were conducted using solutions at various lauric acid concentration levels. Results indicated that in the concentration range investigated (1 x 10⁻⁶ M to 4 x 10⁻⁵ M), adsorption of the ionic species (laurate ions) was independent of the concentration of the acid in the bulk. This is in agreement with the proposed hypothesis that the ionic adsorbate was chemisorbed (coverage up to a "complete" monolayer). Slight increase in the amount of neutral acid adsorbed at pH's above 7.5 with increasing bulk concentration was observed.

(d) **Effect of Added Copper Ions**

Cupric sulphate (1 x 10⁻⁵ M) was added to lauric acid solutions (2 x 10⁻⁵ M) and adsorption onto cupric oxide substrates was studied at various pH's. Evidence for the interaction between lauric acid and copper species in the bulk of the solution were obtained supporting
the hypothesis (Section 4.1) put forward to explain depression of
tenorite flotation by added copper ions. It was assumed that copper
ions depress tenorite flotation by reacting with collector outside
the interface (depletion of effective collector species).

**Acid Solutions**

During tests carried out in acidic solutions, formation of
physically adsorbed layers composed essentially of cupric laurate
(some monomeric acid as secondary component) was observed. Concentration
of the adsorbed species increased substantially with time of exposure
supporting the proposed physical nature of the phenomena. Fig. 55,
spectrum A, shows the spectrum of mirrors exposed to a pH 5.5 solution
for one hour. The intensity of the CH\textsubscript{2} asymmetric stretching band at
2920 cm\textsuperscript{-1} (\(\Delta R = 0.0020\); greater than \(\Delta R = 0.0015\) for a monolayer)
suggested that multilayer adsorption occurred. The COO\textsuperscript{-} asymmetric
(1585 cm\textsuperscript{-1}) and symmetric (1430 cm\textsuperscript{-1}) stretching vibrations assigned
to cupric laurate were the predominant carbonyl bands. The presence
of neutral acid molecules in concentration somewhat higher than those
observed in similar spectra of films formed in the absence of added
copper ions (see Fig. 54, spectrum A) was indicated by the comparatively
stronger 1730 cm\textsuperscript{-1} band. Physical adsorption of copper hydroxo
complexes containing hydrogen bonded monomeric acid molecules can be
postulated to explain the above phenomenon.

Bands associated with chemisorbed species (laurate ions and
monomeric acid) were not evident in spectrum A of Fig. 55. However,
washing the mirrors with organic solvents (30 minutes immersion in
Figure 55. Reflection spectra of lauric acid films adsorbed onto cupric oxide substrates from solutions containing added copper ions ($1 \times 10^{-5}$ M CuSO$_4$; 1 hour exposure): (A) pH 5.5; (B) same as A but spectra recorded after 30 minutes immersion in hexane; (C) pH 8.5.
200 ml of the solvent) removed the physically adsorbed species exposing a chemisorbed layer (spectrum B, Fig. 55) identical to that observed in experiments of part (a) (adsorption in the absence of added copper ions, spectrum A, Fig. 54). The low adhesion of the copper laurate and lauric acid – copper complex molecules to the substrate indicates that these species have been physically adsorbed.

**Basic Solutions**

Formation of multilayers also occurred during adsorption tests conducted at pH's slightly basic (approximately pH 7 to 9). In this case, the presence of cupric laurate was not observed. Physically adsorbed layers contained only monomeric acid molecules, probably hydrogen bonded to cupric hydroxide precipitates. Physical adsorption on top of a chemisorbed layer of monomeric acid (identical to that identified during tests carried out without addition of copper ions; spectrum B, Fig. 54) was indicated by organic solvent tests similar to those mentioned above. Spectrum C, Fig. 55, was recorded after exposing a pair of cupric oxide covered front surface gold mirrors to a pH 8.5 solution for one hour (mirrors became partially hydrophobic). The intensity of the band at 1730 cm⁻¹, associated with the monomeric acid molecule's, appears substantially higher than that observed in spectra of films formed in absence of copper ions and at similar pH's (Fig. 54B). The presence of bands at approximately 3300 and 930 cm⁻¹, in Fig. 55C, frequencies close to the OH stretching and bending vibrations of
cupric hydroxide (see Fig. 24), * seems to support the hypothesis that monomeric acid molecules were present in the adsorbed film, hydrogen bonded to copper hydroxide precipitates. ** In addition, the bands assigned to cupric hydroxide were not observed in spectra of mirrors recorded after treatment with organic solvents (removal of physically adsorbed species) suggesting that their appearance was associated with the presence of the physically adsorbed layers.

(e) Effect of Dissolved Carbon Dioxide

The tests discussed in the preceding parts of this section were conducted using solutions saturated with an inert gas. The effect of the presence of carbon dioxide in the system, and consequently of its hydrolysis products, was investigated by carrying out experiments similar to those aforementioned but now using solutions saturated with a 300 ppm CO₂ in N₂ gas mixture. Results of these tests showed that the presence of carbon dioxide did not change to any great extent the qualitative and quantitative character of the corresponding adsorbed films formed in solutions saturated with the inert gas. The only noticeable difference, caused by the presence of carbon dioxide, in the spectra of adsorbates was

* Other characteristic bands of the cupric hydroxide spectrum were not observed; the relatively strong Cu-OH bending vibration at 680 cm⁻¹ might have been obscured by the presence of the very strong and broad CuO band at 570 cm⁻¹ in Fig. 55C.

** According to the solubility diagram for cupric hydroxide (shown in Fig. 2), precipitation should occur at pH's greater than approximately pH 7, in solutions containing 1 x 10⁻⁵ total dissolved copper.
the appearance of stronger carbonate bands at approximately 1500 cm\(^{-1}\) and 1400 cm\(^{-1}\), when mirrors were treated in basic solutions. The carbonate bands were more pronounced in the spectra of substrates exposed to carbonated solutions containing added copper ions.

The above observations were in agreement with the equilibrium diagram for the system (Fig. B3, Appendix B) and supported the explanation presented in Section 4.1 for pH drifts during flotation tests. pH drifts in flotation tests conducted at basic pH's and in the presence of carbon dioxide were assumed to be caused by reactions of carbonate ions with the cupric oxide surface and with its hydrolysis product.

(f) **Adsorption of Aqueous Lauric Acid onto Cuprous Oxide Substrate**

Adsorption tests conducted using cuprous oxide covered front surface gold mirrors yielded results similar to those obtained during tests on cupric oxide substrates (discussed in parts (a) to (e) above). Spectra of films adsorbed onto cuprous oxide substrates under conditions identical to those used in the aforementioned tests were recorded and compared with the corresponding spectra of films formed on cupric oxide substrate. No major differences were found. To illustrate this, spectra of films formed on cuprous oxide surfaces during a sequence of tests similar to that reported in Fig. 54 for the case of cupric oxide substrate are presented in Fig. 56.

Spectra of films formed in the presence of oxygen (air saturated solutions) were also obtained in the present case of cuprous oxide.
Figure 56. Reflection spectra of cuprous oxide substrates exposed to lauric acid solutions ($2 \times 10^{-5}$ M, no added copper ions). (A) pH 6.0; (B) pH 8.6, (C) pH 10.0.
Results of test in the presence of oxygen were analogous to those using inert gas saturated solutions.

The above results seems to indicate that the cuprous oxide films were overlayed by a thin cupric oxide layer. This is consistent with the equilibrium diagram for the system (Fig. B2, Appendix B) which suggests that under conditions analogous to those used in the present work, the cupric form is more stable than the cuprous form of the oxide.

(II) "In situ" ATR Studies

Infrared ATR spectra of films adsorbed onto cuprous oxide substrate from aqueous (H₂O and D₂O) solutions of lauric acid (2 x 10⁻⁵ M, pH 5.5) were recorded "in situ". Qualitative analysis of the spectra indicated that the composition of the adsorbed film was not altered to any significant extent by the removal of the substrate from the aqueous phase. Laurate ions and monomeric lauric acid molecules were identified as components of the adsorbed films in agreement with the results of the tests conducted using the specular reflection technique (Section 4.2.2 (I)).

H₂O Solution

Fig. 57 shows an "in situ" spectrum obtained using lauric acid solution in H₂O (30 minutes exposure). Besides the bands associated with the substrate, the liquid phase and the teflon seal (see Fig. 30), the following bands were observed and assigned to species present at the interface: 2800-3000 cm⁻¹ region, CH₂ and CH₃ stretching vibrations
Figure 57. "In situ" ATR spectrum: cuprous oxide substrate in $2 \times 10^{-5}$ M lauric acid solution in H$_2$O (30 minutes exposure time).

Figure 58. ATR spectrum of the cuprous oxide substrate after being exposed to H$_2$O solution of lauric acid (dry sample; H$_2$O removed from liquid cell after recording of the spectrum shown in Fig. 57).
of the organic adsorbate; 1730 cm\(^{-1}\), carbonyl vibration of monomeric lauric acid; 1530 cm\(^{-1}\), asymmetric stretching of adsorbed laurate ions; 1400 cm\(^{-1}\), symmetric stretching of the laurate ions; 1460-1400 cm\(^{-1}\), CH\(_2\) and CH\(_3\) bending vibrations and C-OH coupled with OH bending vibrations; and, 1500 cm\(^{-1}\) and 1360 cm\(^{-1}\), probably associated with carbonates. Position and intensity of these bands were not affected by varying the exposure times (up to 2 hours).

Spectra recorded after formation of the carboxylic film and subsequent to removal of the aqueous medium (see Fig. 58) showed that, except for the almost complete absence of the water bands, all the bands present in the "in situ" spectrum (Fig. 57) were preserved. This suggests that the composition of the interfacial organic film was not altered by drying the mirrors.

**D\(_2\)O Solution**

Results of adsorption tests carried out using D\(_2\)O (Figs. 59 and 60) were similar to those presented in the preceding discussion for the case of H\(_2\)O solutions. However, the absence of a strong H\(_2\)O band at 1600 cm\(^{-1}\) in "in situ" spectra recorded using D\(_2\)O permitted the observation of a weak band at 1580 cm\(^{-1}\) (characteristic frequency of the COO\(^{-}\) asymmetric stretching of the cupric laurate molecules). The presence of this band is probably due to the formation of cupric laurate in the outer part of the double layer interface (reaction of physically adsorbed laurate ions with the hydrolysis product of the copper oxide surface). The 1580 cm\(^{-1}\) band disappeared with the removal of the solution (Fig. 60).
Figure 59. "In situ" ATR spectrum: cuprous oxide substrate in $2 \times 10^{-5}$ M lauric acid solutions in D$_2$O (30 minutes exposure time).

Figure 60. ATR spectrum of the cuprous oxide substrate after being exposed to D$_2$O solution of lauric acid (dry sample, D$_2$O removed from liquid cell after recording of the spectrum shown in Fig. 59).
SUMMARY AND CONCLUSIONS

The flotation behaviour of copper oxide minerals and the mechanisms of adsorption of ionic collectors on copper oxide substrates were investigated, using micro flotation tests and infrared spectroscopy. A highly sensitive specular reflection spectroscopic technique was employed for qualitative and quantitative analyses of adsorbates at surface concentration levels never before attempted in this system. "In situ" infrared spectra of the cuprous oxide/aqueous lauric acid were recorded. The results led to the following major conclusions, listed below.

(1) Adsorption of ionic collectors and floatability of copper oxides are greatly dependent on mineral surface charge.

(2) The "ion adsorption theory" can explain the mechanism of collection of copper oxide minerals by lauric acid: laurate ions are chemisorbed as counter ions in the internal part of the electrical double layer. Monomeric lauric acid molecules are also present in the adsorbed films but their role in the collection process is assumed of secondary importance.

(3) In the presence of excess copper ions, laurate species interact with copper hydroxo complexes in the bulk of the solution depleting the concentration of effective collector species and consequently depressing flotation.

(4) The behaviour of specular reflection spectra of organic films can be explained by the Francis and Ellison theory and give useful information on molecular orientation. Band intensities in spectra of isotropic
films are closely described by equation [8] using optical constants available in the literature for similar bulk compounds. For the case of anisotropic films, band intensities are highly dependent on the orientation of the molecules. However, equation [8] is still applicable provided that orientation effects on the probability that a molecule (or group) will undergo a transition are taken into account.

(5) For the particular case of films adsorbed onto copper oxide substrates from aqueous lauric acid solutions, the composition of the chemisorbed layer is not altered by the removal of the substrate from the aqueous phase.
SUGGESTIONS FOR FURTHER WORK

(1) In the present work, interactions of copper oxides with simple ionic collectors have been investigated. Similar studies carried out on other oxidized minerals of copper and in the presence of different reagents might contribute to a better understanding of the problem of flotation of oxidized copper minerals.

(2) Up to 15 monolayers of stearic acid have been deposited on cupric oxide substrate according to the Langmuir-Blodgett method and their specular reflection spectra recorded. Analogous spectroscopic studies on films containing a much higher number of layers of stearic acid (or other surfactants) deposited on various substrates might yield results useful to the development of the theories of reflection spectroscopy. Also, a better understanding of the characteristics of monolayers transferred to the solid surfaces might be achieved.

(3) "In situ" infrared spectra of the cuprous oxide/aqueous lauric acid interface have been recorded. Application of the technique for recording IR spectra of other interfaces might be possible. Optimum conditions must be experimentally determined for each system.
APPENDIX A

Solubility Data for Selected Organic Compounds

I. Solubility products at 20°C (values refer to infinite dilution and are negative logarithms of solubility products):

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Solubility Products</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lauric acid</td>
<td>5.3</td>
<td>(123)</td>
</tr>
<tr>
<td>Lauryl amine</td>
<td>3.4(at 25°C)</td>
<td>(124)</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>13.8</td>
<td>(65)</td>
</tr>
<tr>
<td>Sodium stearate</td>
<td>6.2</td>
<td>(65)</td>
</tr>
<tr>
<td>Cupric stearate</td>
<td>23.0</td>
<td>(65)</td>
</tr>
<tr>
<td>Oleic acid</td>
<td>12.3</td>
<td>(65)</td>
</tr>
<tr>
<td>Sodium oleate</td>
<td>5.7</td>
<td>(65)</td>
</tr>
<tr>
<td>Cupric oleate</td>
<td>19.4</td>
<td>(65)</td>
</tr>
</tbody>
</table>

II. Solubility in water (mg/1 of water):

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Temperature</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20°C</td>
<td>25°C</td>
</tr>
<tr>
<td>Lauric acid</td>
<td>55</td>
<td>63</td>
</tr>
<tr>
<td>Lauric acid</td>
<td>4.6</td>
<td></td>
</tr>
<tr>
<td>Lauryl amine</td>
<td></td>
<td>42</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>2.9</td>
<td>3.4</td>
</tr>
</tbody>
</table>

III. Solubility in organic solvents at 20°C (g/100 g of solvent).

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Solvents</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Methanol</td>
<td>Acetone</td>
</tr>
<tr>
<td>Lauric acid</td>
<td>120</td>
<td>60.5</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>0.1</td>
<td>1.5</td>
</tr>
</tbody>
</table>
APPENDIX B

Equilibrium Diagrams

Figure B1. Stability of copper compounds as functions of partial pressures of oxygen ($P_{O_2}$) and carbon dioxide ($P_{CO_2}$), at 25°C and 1 atmosphere total pressure. Pure liquid water is assumed present (ref. 125).
Figure B2. Potential (Eh)-pH equilibrium diagram for the system Cu-H₂O-O₂ at 25°C and 1 atmosphere total pressure. (Ref. 125).
Figure B3. Potential (Eh)-pH equilibrium diagram for the system Cu-H₂O-O₂=CO₂-S at 25°C and 1 atmosphere total pressure. Partial pressure of carbon dioxide (P_{CO₂}) = 10^{-3.5} (typical content in air). Total dissolved sulfur species = 0.1 M. (Ref. 125).
Figure B4. Logarithmic concentration diagrams for carbonate species in aqueous solution in equilibrium with $10^{-3.5}$ atmosphere partial pressure of carbon dioxide ($P_{CO_2}$), at 25°C (Equilibrium constants from Ref. 126).

\[
[CO_2]_{aq} = 3.43 \times 10^{-2} \ p_{CO_2}
\]

\[
[HCO_3^-] = 1.7 \times 10^{-4} \frac{[H_2CO_3^-]}{[H^+]}\]

\[
[H_2CO_3] = 2.6 \times 10^{-3} \ [CO_2]_{aq}\]

\[
[CO_3^{2-}] = 5.6 \times 10^{-11} \frac{[HCO_3^-]}{[H^+]}\]

\[
[OH^-]\]
APPENDIX C

Characteristic Group Frequencies

1. Conditions governing data in table of selected characteristic group frequencies.
   i) Characteristic absorption frequencies of groups most pertinent to this work are presented in the form of a table (pages 159 to 162).
   ii) Unless otherwise stated, the bands usually appear within $\pm 10 \text{ cm}^{-1}$ of the position shown in the table.
   iii) Notation: $\nu =$ stretching vibration; $\delta =$ bending vibration; $\text{as} =$ asymmetric; $s =$ symmetric.
   iv) General references: 127, 128, and 114. Other references: as stated in brackets ( ).
### 2. Table C

Selected Characteristic Group Frequencies

<table>
<thead>
<tr>
<th>Group</th>
<th>Band (cm(^{-1}))</th>
<th>Assignment</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>-CH(_3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2960</td>
<td>(\nu) as</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2870</td>
<td>(\nu) s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1460-1450</td>
<td>(\delta) as</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1380</td>
<td>(\delta) s</td>
<td></td>
</tr>
<tr>
<td>-CH(_2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2925</td>
<td>(\nu) as</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2850</td>
<td>(\nu) s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1465</td>
<td>scissoring</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1350-1180</td>
<td>wagging and twisting</td>
<td>Regular series of bands in fatty acids and soaps (band progression).</td>
</tr>
<tr>
<td></td>
<td>720</td>
<td>((\text{CH}_2)_n) rocking</td>
<td></td>
</tr>
<tr>
<td>O-H free</td>
<td>3700-3500</td>
<td>(\nu)</td>
<td>Sharp band in cupric hydroxide (85): 3580 cm(^{-1}). In monomeric carboxylic acids: 3560-3500 cm(^{-1}) (127).</td>
</tr>
<tr>
<td></td>
<td>(\sim)1250</td>
<td>(\delta) (in-plane)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\Delta)225</td>
<td>(\delta) (out-of-plane)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3200-2500</td>
<td>(\nu)</td>
<td>Chelate compounds. Broad.</td>
</tr>
<tr>
<td>O-H inter-molecular hydrogen bond</td>
<td>3550-3450</td>
<td>(\nu)</td>
<td>Single-bridge compounds. Sharp. In dilute solutions of carboxylic acids in dioxane: (\sim)3100 cm(^{-1}); due probably to the complex</td>
</tr>
</tbody>
</table>
Table C (Cont.)

<table>
<thead>
<tr>
<th>Group</th>
<th>Band (cm(^{-1}))</th>
<th>Assignment</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3400-3200</td>
<td>(\nu)</td>
<td>-Polymeric association. Broad. Water of crystallization; also at 3600-3100 cm(^{-1}). In malachite: 3430 cm(^{-1}) (129). In copper hydroxide: 3310 cm(^{-1}) (130). In deuterium oxide: O-D stretching at 2530 cm(^{-1}) (131).</td>
</tr>
<tr>
<td>O-H intermolecule hydrogen bond (cont.)</td>
<td>1500-1300</td>
<td>(\delta) (in-plane)</td>
<td>-Broad. Frequently two. Shifted to higher frequencies with stronger hydrogen bond. In dimeric carboxylic acids: 1430, 1410 and 1300 cm(^{-1}) (coupled with C-OH stretching modes) (132).</td>
</tr>
<tr>
<td></td>
<td>(\approx)650</td>
<td>(\delta) (out-of-plane)</td>
<td>-Broad. Higher frequencies with stronger hydrogen bonds. In dimeric carboxylic acids: 935 + 15 cm(^{-1}). Monomeric acids do not show OH (\delta) (out-of-plane) (133). -O-H bending in liquid water: 1650-1600 cm(^{-1}) (87). In malachite: 1050, 880 and 780 cm(^{-1}) (86). In azurite: 957, 841 and 772 cm(^{-1}) (86). In copper hydroxide: 940 cm(^{-1}) (85). -O-D bending in deuterium oxide: 1210 cm(^{-1}) (87).</td>
</tr>
<tr>
<td>C-OH</td>
<td>1430-1030</td>
<td>(\nu)</td>
<td>-In monomeric carboxylic acids: 1375 cm(^{-1}) (117). In dimeric acids: 1430, 1410 and 1300 cm(^{-1}) (coupled with OH(\delta)(out-of-plane) modes).</td>
</tr>
</tbody>
</table>
Table C (Cont.)

<table>
<thead>
<tr>
<th>Group</th>
<th>Band (cm(^{-1}))</th>
<th>Assignment</th>
<th>Remarks</th>
</tr>
</thead>
</table>
| C=O   | 1900-1580           | \(\nu\)    | -Saturated ketones: 1715 cm\(^{-1}\)  
Saturated aldehydes: 1730 cm\(^{-1}\)  
Saturated esters: 1735 cm\(^{-1}\)  
Saturated carbonates: 1750 cm\(^{-1}\)  
Saturated carboxylic acids: monomer (in carbon tetrachloride): 1760 cm\(^{-1}\) (114); monomer (in dioxane): 1735 cm\(^{-1}\) (114); dimer: 1710-1700 cm\(^{-1}\)  
single-bridge acids, \(\ldots\) \(\text{OH}\ldots\) \(\text{OH}\ldots\): 1715 cm\(^{-1}\) (115).  
-In dimeric carboxylic acids: 680 (134). |
|       |                     |            |         |
| C-Cl  | 800-600             |            | -In carbon tetrachloride: 784 and 764 cm\(^{-1}\). |
| C-F   | 1400-1000           |            | -In teflon: 1219 and 1149 cm\(^{-1}\). |
| CO\(_3\) | 1450-1410 \(\nu\)  |            | -In basic carbonates absorption in the region 1430 cm\(^{-1}\) is almost always doubled. A series of bands appear between 1110 and 700 cm\(^{-1}\). Malachite shows four bands in the region 1550-1350 cm\(^{-1}\). |

\(v\) as, \(v\) s
Table C (Cont.)

<table>
<thead>
<tr>
<th>Group</th>
<th>Band (cm(^{-1}))</th>
<th>Assignment</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_3^−)</td>
<td></td>
<td></td>
<td>These are: 1520, 1500, 1426, and 1393 cm(^{-1}). Other malachite bands due to the carbonate ion are: 1095, 823 and 713 cm(^{-1}). Azurite shows the following carbonate bands: 1505, 1470, 1424, 1094, 823, and 747 cm(^{-1}) (130). -Bicarbonates do not absorb in the 1430 cm(^{-1}) region. Instead two widely separated bands appear on either side (127).</td>
</tr>
<tr>
<td></td>
<td>(cont.)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S(_4^−)</td>
<td>1130-1080</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>680-610</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silicates</td>
<td>1100-900</td>
<td>-Quartz</td>
<td></td>
</tr>
<tr>
<td>Cu-OH</td>
<td>680</td>
<td>δ</td>
<td>-Strong (129).</td>
</tr>
<tr>
<td>Cuprous oxide</td>
<td>623-609</td>
<td>lattice vibrations</td>
<td>-(84,85,90,135,136).</td>
</tr>
<tr>
<td>Cupric oxide</td>
<td>510</td>
<td></td>
<td>-(85).</td>
</tr>
</tbody>
</table>
Determination of the IEP of Tenorite

The IEP of tenorite (reagent grade cupric oxide, Fisher C 474, used in the flotation tests) was estimated at pH 9.4 using Mular and Roberts method (103). The tenorite was stage ground in an agate mortar and 10 samples weighing 1 gm were placed in 100-ml beakers each containing 50 ml of 0.01 N Na$_2$SO$_4$ solutions. The pH (pH$_i$) was adjusted with NaOH. The ionic strength was raised to 10$^{-1}$ by adding the required amount of the supporting electrolyte (Na$_2$SO$_4$). The final pH (pH$_f$) was measured after stirring the solution with a glass rod for three minutes. Values of ΔpH = pH$_i$ - pH$_f$ are plotted against pH$_f$ in Fig. D.
Figure D. $\Delta \text{pH}$ versus $\text{pH}_f$ for tenorite (IEP determination based on Mular and Roberts method).
APPENDIX E

Calibration of the Torsion-Wire Langmuir Balance

The "calibrating weights method", described in Ref. 77 was used for the calibration of the balance. The torsion-wire was a 10" monel wire, 15 cm long.

w grams of the calibrating weight require the torsion head to be rotated \( \theta \) degrees to return the float to the zero position. The sensitivity \( S \) (dynes.cm\(^{-1}\).degree\(^{-1}\)) of the balance is given by:

\[
S = \frac{wg l_c}{\theta l_f L},
\]

where \( l_c = 7.0 \) cm, is the lever arm for the calibrating weight (horizontal distance from the weights to the wire); \( l_f = 12.5 \) cm, is the lever arm for the float (vertical distance from the float to the wire); \( L = 14.0 \) cm, is the effective length of the float (taken to be the length of the float plus half the width of the gaps at its end); \( g = 980.6 \) cm.sec\(^{-2}\), is the acceleration of gravity.

A plot of \( w \) versus \( \theta \) (Fig. E) gives:

\[
\frac{w}{\theta} = 5.3 \times 10^{-3} \text{ gm. degree}^{-1}
\]

Using formula El and the values of the parameters given above, the sensitivity of the balance is calculated as \( S = 0.21 \) dynes.cm\(^{-1}\).degree\(^{-1}\): a pressure of 1 dyne.cm\(^{-1}\) corresponds to 4.76° rotation angle of the torsion head.
Figure E. Torsion-wire Langmuir balance calibration curve.
APPENDIX F
Typical Behavior of Stearic Acid Films Spread at the Air-Water Interface

An example of the experimental data obtained during compression of stearic acid monolayers in the Langmuir trough is presented in Fig. F (pressure-area curve) and Table F (numerical values used for plotting Fig. F curve).

The area occupied by a molecule of stearic acid in the solidified film was measured at 20.9 Å². This is in good agreement with literature values of 20.4 Å² obtained for stearic acid monolayers spread under similar conditions (77).
Figure F. Pressure-area curve for a typical stearic acid monolayer. 
\((24^\circ C, 10^{-4} \text{ N } \text{H}_2\text{SO}_4; \text{ pH } 4.4)\).
<table>
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<tr>
<th>Measured area (a) of the film (cm²)</th>
<th>Area occupied by one molecule (a x 10^{16}/2.7 x 10^{17} A²)</th>
<th>θ (measured within ± .1 degree)</th>
<th>Surface Pressure (θ x .21) in dynes.cm⁻¹</th>
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APPENDIX G

Calculation of $\Delta R_{\text{as,CH}_2 \text{ random}}$

Let it be assumed that a "monolayer" of stearic acid presenting the properties given below can be formed on the surface of a solid.

(i) The CH$_2$ groups of the molecules lie in planes randomly oriented with respect to the solid surface. Such a hypothetical film would have isotropic optical properties and equation [8], Chapter II (Francis and Ellison theory) describes the relation between band intensity and film thickness.

(ii) The thickness (d) of the "monolayer" (concentration term in the expression of $\Delta R$) is "equivalent" to that of a solidified monolayer at the air-water interface (d = 24.4 Å as reported by Blodgett in Ref. 137).

(iii) The refractive index ($N_1$) of the film at the band maximum (2920 cm$^{-1}$) is approximately the same as the refractive index ($n_D$) of bulk stearic acid ($N_1 = n_D = 1.4299$; sodium light, 25°C, Ref. 138).

(iv) The molecular extinction coefficient ($\varepsilon_{(2920 \text{ cm}^{-1})}$) of the stearic acid molecules in the film is approximately equal to the molecular extinction coefficient of CH$_2$ groups (times 16) in bulk organic compounds ($0.125 \times 10^{-18} \text{ cm}^2$ per group, Ref. 139). The absorption constant ($K_1$) for the stearic acid molecules in the film can be calculated from the value of $\varepsilon_{(2920 \text{ cm}^{-1})}$ in the following way.

$$\varepsilon_{(2920 \text{ cm}^{-1})} = 16 \times 0.125 \times 10^{-18} = 2 \times 10^{-18} \text{ cm}^2 \text{ per molecule}$$

$$\alpha_{(2920 \text{ cm}^{-1})} = 2.303 \times \rho \times \varepsilon_{(2920 \text{ cm}^{-1})} \text{ (expression [4], Chapter II)}$$
\[ \rho = \text{density} \times \text{Avogadro's number/molecular weight} \]

\[ \rho = 0.9408 \times 6.022 \times 10^{23}/284.5 \text{ (values from Ref. 138)} \]

hence,

\[ \alpha(2920 \text{ cm}^{-1}) = 9.17 \times 10^{-3} \text{ cm}^{-1} \]

and,

\[ K_1 = \frac{\alpha(2920)}{4\pi} = 0.25 \text{ (} \lambda = 1/2920 = 3.42 \times 10^{-4} \text{ cm}). \]

By substituting the values of \( d = 24.4 \text{ Å} \), \( N_1 = 1.4299 \), \( K_1 = 0.25 \), \( \theta = 70^\circ \) and \( \lambda = 3.42 \times 10^4 \text{ Å} \) in equation [8], \( \Delta R \) for the CH\(_2\) asymmetric stretching band in a hypothetical specular reflection spectrum of a monolayer composed of randomly oriented stearic acid molecules can be calculated as

\[ \Delta R_{\text{as,CH}_2 \text{ random}} = 0.0079. \]
APPENDIX H

Calculation of a Theoretical Value for $\Delta R_{\text{as}, \text{CH}_2 \perp} / \Delta R_{\text{as}, \text{CH}_2 \text{ random}} = r$

Let $P_1$ be the probability that a stretching vibration mode of CH$_2$ groups lying in planes normal to the surface will interact with the component of the electric field ($E_{//,z}$) parallel to the plane of incidence of the radiation. Call $P_2$ the probability in the case of randomly oriented CH$_2$ groups. As discussed in Chapter II.

$$\Delta R_{\text{as, CH}_2 \perp} \sim P_1, \text{ and } \Delta R_{\text{as, CH}_2 \text{ random}} \sim P_2$$

It follows that

$$r = \frac{P_1}{P_2}$$

From expression [9], Chapter II:

$$P_1 = \frac{4\pi}{h^2} \frac{\mu_{1z}^2}{\mu_{1z}} E_{//,z}^2$$

$$P_2 = \frac{4\pi}{h^2} \frac{\mu_{2z}^2}{\mu_{2z}} E_{//,z}^2$$

therefore,

$$r = \left(\frac{\mu_{1z}}{\mu_{2z}}\right)^2 \quad [H1]$$

where, $\mu_{1z}$ is the component (normal to the surface) of the matrix element
of the dipole moment change for the stretching vibration mode of \( \text{CH}_2 \) groups lying in planes normal to the surface, and \( \mu_{2z} \) is the average value for the normal components of the matrix element of the dipole moment change in the case of randomly oriented groups. Considering that for randomly oriented molecules the component of the matrix element can form angles with the solid surface varying from zero to \( \pi \) radians, this average value can be expressed as

\[
2z = \frac{\int_{0}^{\pi} \mu_{1z} \sin \theta \, d\theta}{\pi} = \frac{[-\mu_{1z} \cos \theta]_{0}^{\pi}}{\pi} = \frac{2}{\pi} \mu_{1z}
\]

Hence,

\[
r = \left( \frac{\mu_{1z}}{\frac{2}{\pi} \mu_{1z}} \right)^2 = 2.46
\]
APPENDIX I
Measurement of Copper Oxide Film Thickness from ΔR Values

The thickness (d) of an isotropic film is expected to be directly proportional to the measured ΔR values of the specular reflection spectra of the film. Equation [8] (Francis and Ellison) can be written:

\[ d_{A^\circ} = x \cdot ΔR \]

where

\[ x = \frac{\lambda N_1^2 \cos \theta}{16 \pi \sin^2 \theta K_1} \]

Estimating x

(i) Cuprous oxide film

x can be calculated using \( N_1 \) and \( K_1 \) values given by O'Keefe \(^{90} \)

\( (N_1 = 1.5; \ K_1 = 0.75, \text{ at } 645 \text{ cm}^{-1}) \). \( \theta = 70^\circ, \ \lambda = 15.5 \mu = 1.55 \times 10^5 \text{ Å}^\circ \), therefore, \( x = 5,600 \text{ Å}^{-1} \), and

\[ d_{A^\circ} = 5,600 \ \Delta R_{645 \text{ cm}^{-1}} \]  \[ \text{[11]} \]

(ii) Cupric oxide film

Since values of \( N_1 \) and \( K_1 \) (at 570 cm\(^{-1}\)) for cupric oxide films were not available, x was determined from a plot (Fig. I) of \( d_{A^\circ} \) obtained by independent thickness measurements (interferometry) versus observed \( \Delta R_{570 \text{ cm}^{-1}} \) values. From Fig. I, x = slope = 6,400 Å\(^{-1} \), hence,

\[ d_{A^\circ} = 6,400 \ \Delta R_{570 \text{ cm}^{-1}} \]  \[ \text{[12]} \]
Figure I. Relation between cupric oxide film thickness and intensity of CuO reflection band at 570 cm$^{-1}$. 

$x = 6,400$ (Å$^{-2}$)
APPENDIX J

Calculation of Angles Formed by Planes Containing CH$_2$ Groups of Stearic Acid Monolayers with the Solid Surface

An expression (similar to equation H$_1$, Appendix H) can be obtained, on the basis of the Francis and Ellison theory, for the ratio

$$\frac{\Delta R_{as, CH_2}}{\Delta R_{as, CH_2 \; random}} = r,$$

where $u_{3z}$ is the component (normal to the surface) of the matrix element of the dipole moment change for the stretching vibration mode of the CH$_2$ groups lying in planes forming $\theta$ (unknown) degrees with the surface, and $u_{2z} = \frac{2}{\pi} u_{1z}$ as given in Appendix H.

$$u_{3z} = u_{1z} \sin \theta,$$

thus,

$$r = \left( \frac{u_{1z} \sin \theta}{\frac{2}{\pi} u_{1z}} \right)^2, \text{ and } \theta = \sin^{-1} \left( \frac{2}{\pi} r^{1/2} \right) \quad [J1]$$

Expression J1 was used to calculate the average angle made by planes containing CH$_2$ groups of stearic acid molecules with the solid surface, in films deposited on cupric oxide substrates according to the Langmuir-Blodgett method; r values were obtained by dividing average $\Delta R$ values given in Table 4 by 0.0079 ($\Delta R_{as, CH_2 \; random}$ for a hypothetical monolayer as calculated in Appendix G).
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