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Internal Reflection Spectra of Surface Compounds and Adsorbed Molecules

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The application of attenuated total reflection (ATR) spectroscopy in surface studies of inorganic adsorbents and catalysts, polymers, and optically transparent electrodes is discussed. The basic principles of ATR spectroscopy as applied to surface phenomena are considered, with special reference to thin films, industrial adsorbents and catalysts, and polymer degradation processes. 276 References.

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I. INTRODUCTION

Since the first report (Fahrenfort, 1961) of spectral measurements on a condensed phase by attenuated total internal reflection[1] the ATR (attenuated total reflection) method has been widely used in practical spectrochemical studies[2-5].

The basic principles of attentuated total reflection spectroscopy and of its applications have already been discussed in monographs[5,6] and reviews[7-13]. The rapid development of practical applications was helped by the discovery of high refractive index materials transparent in the infra-red, by new mathematical methods of describing the ATR spectra, and by the appearance of special attachments for all types of i.r. spectrometer, allowing single (ATR) and multiple (MATR) internal reflection. The wide appeal of the method is explained also by the similarity between the ATR and the transmission spectra, both in the position of the bands and in the validity of Beer's law.

However, in spite of the outward similarity between ATR and transmission spectra, there is a fundamental difference, associated with the form of the electromagnetic field interacting with the sample. When the spectrum is recorded under ATR conditions the electric vector of the light wave near the interface between the sample and the prism retains all its three components, and as a result the ATR spectra (unlike the transmission spectra) give information on the dipoles oriented at right angles to the surface. Hence, the surface and the bulk properties of solids can be studied simultaneously by the combined use of ATR and transmission spectra.

A large amount of experimental information on surface phenomena obtained by the ATR method is now available. New variants of internal reflection spectroscopy include spectrorefractometry, Raman spectroscopy, liquid ATR spectroscopy, studies of chemical reactions and of adsorption on flat surfaces, and the use of optically transparent electrodes in electrochemistry. New develoments in methods of obtaining the ATR spectra of surfaces and in the study of surface compounds and of adsorption on sorbents, catalysts, polymer surfaces, and electrodes are reviewed in this paper.

II. BASIC PRINCIPLES OF THE ATTENUATED INTERNAL REFLECTION SPECTROSCOPY METHOD

The ATR spectra are produced by the high sensitivity of the reflection coefficient R to changes in the absorption coefficient κ and, to a smaller extent, in the refractive index n. By optimising the experimental conditions we can minimise the sensitivity of the spectra to changes in n while retaining their sensitivity to changes in κ. This is achieved by suitable choice of the angle of incidence: a few degrees greater than the critical angle ($\sin\theta_{crit} = n_2/n_1$, where n_2 is the refractive index of the unknown material and n_1 is the refractive index of the ATR attachment, with $n_1 > n_2$). The spectra recorded with $\theta > \theta_{crit}$ show very little distortion of the bands, though the intensity of the bands is greatly reduced. Stronger bands can be obtained by increasing the number of reflections: the method is then called the MATR (multiple attenuated total reflection) method. The spectra measured with $\theta \cong \theta_{crit}$ can differ very substantially from the absorption spectra, but they offer a high contrast even after a single reflection. The choice of the method of producing the spectrum (ATR or MATR) depends on the specific features of the problem.

1. Principles of Quantitative Analysis by ATR Spectroscopy

Quantiative analysis by ATR spectroscopy consists in determining the optical constants n and κ from the ATR spectra of the experimental materials by using the Fresnel formulae. The spectra obtained from multi-layer systems, or substances having a surface layer of variable concentration, can be analysed by using the generalised Fresnel formulae sometimes called the recursion formulae[14,15]. Since the calculation can be carried out on a computer the use of the recursion formulae offers a flexible method of quantitative analysis in ATR spectroscoy, because most surface concentration profiles can be modelled as multi-layer systems on a computer. Various approximations are used in analytical practice to describe the dependence of the reflectance coefficient R on the absorption (or on the concentration) by means

of simple expressions. These approximations are obtained by expanding the R coefficient in a power series of the adsorption coefficient κ.[16] The expression proposed by Harrick[5] is the simplest and the most widely used.

The reflectance coefficient R under conditions of internal reflection can be expressed as

$$R = 1 - \alpha d_{\text{eff}},$$

where $\alpha = 4\pi\kappa\nu$ is the absorption coefficient, and d_{eff} is the effective thickness. At low absorptions ($\alpha d_{\text{eff}} < 0.1$) this expression is equivalent to approximating R by a series expansion in α truncated after the first term. Hence, since the attenuation of the light intensity after a single reflection is small, the experimetnally measured reflectance coefficient can be expressed as

$$R = e^{-\alpha d_{\text{eff}}}.$$

For large samples, of thickness much greater than the wavelength of the light ($2\pi d/\lambda_1 > 1$), we have the following expressions for parallel and for perpendicular polarisation of the incident light respectively:

$$\frac{d^{\perp}_{\text{eff}}}{\lambda_1} = \frac{n_{21}\cos\theta}{\pi(1-n_{21}^2)\cdot(\sin^2\theta - n_{21}^2)^{1/2}} \qquad \frac{d^{\parallel}_{\text{eff}}}{\lambda_1} = d^{\perp}_{\text{eff}} \cdot \frac{2\sin^2\theta - n_{21}^2}{(1-n_{21}^2)\sin^2\theta - n_{21}^2},$$

where $n_{21} = n_2/n_1$ is the relative refractive index. In both cases the effective thickness decreases as θ increases, and increases with the wave length of the light in the optically denser medium ($\lambda_1 = \lambda/n_1$).

Several authors have used the Beer–Lambert law in spectro-analytical ATR work. Calibration curves (optical density against concentration) were used to analyse polyester layers[17,18], for the quantitative determination of vinyl acetate in the polyethylene copolymer[19] used as a surface-active additive to Nylon-6,[20] to monitor the extent of reaction during the synthesis of epoxy resins[21], and for the quantitative determination of carbonyl compounds in polyethylene[22].

In the case of a thin film on a transparent substrate (n_3), and assuming that the conditions $2\pi d/\lambda_1 < 0.1$ and $\kappa < 0.1$ apply, the effective thicknesses can be obtained to a good approximation from the expressions

$$d^{\perp}_{\text{eff}} = \frac{4n_{31}d\cos\theta}{1-n_{31}^2}, \qquad d^{\parallel}_{\text{eff}} = d^{\perp}_{\text{eff}} \frac{(1+n_{32}^4)\sin^2\theta - n_{31}^2}{(1+n_{31}^2)\sin^2\theta - n_{31}^2}.$$

By comparing the expressions for thick samples and for thin films we note that the ATR spectra of thin films are similar in many ways to ordinary transmission spectra. Thus, their intensity is independent of the wave length, and in the neighbourhood of the critical angle the changes in d_{eff} are gradual. In thin films $d^{\perp}_{\text{eff}}$ can be greater than or smaller than $d^{\parallel}_{\text{eff}}$, depending on the relative values of n_1 and n_2, and both these parameters can be substantially greater than the geometric thickness of the sample.

The spectral changes in the absorption coefficient α can be found by measuring R. The integral characteristics of the bands also are calculated from the ATR spectra, using the more convenient Γ-integral (related to the usual A-integral ($A = \int \alpha d\nu$) by the simple expression $\Gamma = A\nu_{\max}$)[23]. Since $\alpha = Kc$, where K is the molecular absorption coefficient and c is the concentration, we have

$$R = e^{-Kcd'_{\text{eff}}/\nu},$$

where $d'_{\text{eff}} = d_{\text{eff}}\nu \cdot n_1$. Therefore we can write

$$\Gamma = \int \alpha \frac{1}{\nu} d\nu = \frac{1}{cd'_{\text{eff}}} \int \ln\frac{1}{R} d\nu.$$

If the Γ-integral is expressed in the dimensions of cm^2 $mole^{-1}$ the intensity of the fundamental vibrations lies in the range 10^2–10^5, and that of the overtones in the range 1–100.

In practice the Kramers–Kronig method[24] is used most often to evaluate n and κ, because it requires only half as many measurements as the two-angle method[5]. The Kramers–Kronig calculations rely on reference values ("tie-values") of n and κ, known for one or two points in the integration region:

$$\varphi(\nu_0) = -\frac{\nu_0}{\pi}\int_{\nu_{\text{init}}}^{\nu_{\text{fin}}} \frac{\ln R(\nu)}{\nu^2 - \nu_0^2} + C_1(\nu_0) + C_2(\nu_0),$$

where ν and ν_0 are the time-dependent and the fixed wave number, ν_{init} and ν_{fin} are the limits of the integration range, and C_1 and C_2 are correction terms[24]. Having calculated $\phi(\nu_0)$ we can find the "amplitude" reflection coefficient

$$\hat{r}(\nu_0) = R^{1/2} e^{i\varphi(\nu_0)},$$

which is related to n and κ (for perpendicular polarisation) by the expression

$$\hat{r}_{\perp} = \frac{(\bar{n}_2^2 - n_1^2\sin^2\theta)^{1/2} - n_1\cos\theta}{(\bar{n}_2^2 - n_1^2\sin^2\theta)^{1/2} + n_1\cos\theta},$$

where $\bar{n}_2$ is the complex refractive index of the material ($\bar{n}_2 = n_2 - i\kappa_2$). The first attempt to measure n_2 and κ_2 from ATR infrared spectra by this method[11] gave satisfactory results.

Some regions of the spectrum of fused quartz[25] are shown in Fig.1 to illustrate the comparison of bulk and surface properties in terms of measurements of optical constants by different methods. The absorption by the surface layers of SiO_2, given by the ATR measurements, is quite different from the bulk optical properties of quartz. The results shown in Fig.1 are qualitatively consistent with measurements on a quartz sample in optical contact with a Ge ATR cell, and with measurements by the liquid technique[68].

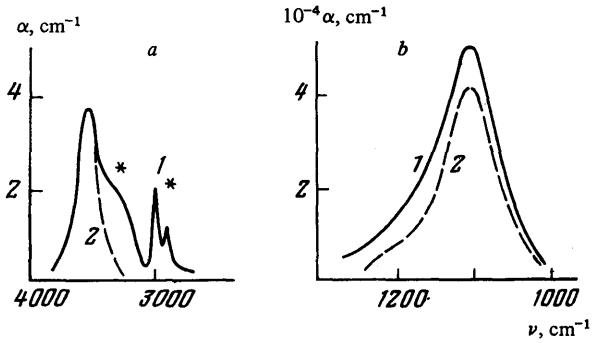


Figure 1. Optical properties of polished fused quartz, measured by different methods: (*a*) *1*) ATR method, *2*) transmission method; (*b*) *1*) ATR method, *2*) external reflection method. The asterisks denote bands due to adsorbed water and hydrocarbons.

Direct quantiative studies of substances supported on solid surfaces are complicated by the need for an ideal contact between the sample and the ATR cell (which is readily achieved in the case of liquid samples). Some workers assume that a "physical contact" is adequate for measurements of n

and κ, others make a correction for the transition layer (or gap) by using an intermediate value of the refractive index[26–28]. In some cases "optical contact" between the surfaces is successfully established, giving reliable measurements on strong bands, but is is claimed[29] that a gap of 40–100 Å is still present, though it does not substantially affect the measurements if the material which fills the gap by capillary condensation (usually water) is transparent in the chosen spectra region. In the case of measurements in the absorption band of the adsorbate (i.e. in the transmission region of the substrate material) even such a small gap can produce unexpected results, since the topography of the surface will produce a gap at the contact between the two solid surfaces, and as a result of capillary forces this gap will contain a thin layer of water and hydrocarbons. These effects are more marked when the surfaces are etched.

The possibility (in principle) of obtaining accurate values of n and κ from a solid surface can be realised in practice by using liquid ATR spectroscopy in the visible[5] or the i.r. region[30]. This variant has been used to study pentacene films adsorbed on crystalline or glassy substrates, and also the surface properties of poly(tetrafluoroethylene) (Teflon-4) in thin-film and in massive samples[30]. Immersion liquids having a specially high refractive index have proved very useful in this work.

An important practical contribution to this type of measurement was a detailed study[31] of the dependence of the results on the quality of the optical contact and on the size of the air gap beween the polymer sample and the MATR cell, with a description of an attachment for pressing the sample controllably against the cell. An apparatus including such an attachment is described also in Ref.32.

Modified variants of ATR spectroscopy have been used in recent years (in addition to the more traditional ATR methods) to study solid surfaces[33–35]. In all these variants a gap, usually air-filled, is present between the sample and the ATR cell when a spectrum is recorded from a flat surface. Under these conditions the incident light interacts with surface vibrations (polaritons) which are non-radiative, i.e. they are not detected under normal conditions such as in transmission spectra. Studies of the spectroscopic characteristics of polaritons give information on the dynamics of the crystal lattice. Experiments of this type, with alkali halide crystals, were first reported in Ref.36. The method was used also to study the surface of a series of uniaxial crystals[37], including α-quartz[38,39].

In studies of finely divided media by the ATR method surface polariton bands can appear in the spectrum close to strong bands from the crystalline powder[40]. The intensity and shape of the latter will be largely determined by the crystal habit of the particles and by the polarisation of the incident light. It has been shown[40,41] that whereas external reflectance spectra consist mainly of bands from transverse vibrations of the crystal lattice the ATR spectra tend to reveal longitudinal and surface vibrations. It should be noted that the study of adsorption on powders not previously treated (e.g. by pressing) requires a large number of reflections (50–100), as well as an expanded photometric scale.

In work with relatively coarse particles distortion of the bands (or even the appearance of new bands) is possible, and model calculations of the reflectance spectra must be carried out to avoid incorrect interpretation of the experimental results. Thus, a simple multi-layer model has been used[41] to calculate the ATR spectra of powders and fibres from the Fresnel formulae for multi-layer systems[14]. The effective reflectance coefficient R of such a system for a plane wave can be expressed as a statistical sum in the case of cylindrical fibres. It is assumed that the optical properties of each layer are equivalent to those of one fibre. If the diameter of the fibre is $d \gg \lambda$, and $\theta \gg \theta_{crit}$, the integration can be replaced by a summation with $\theta = \text{const}$.[44]

A convincing test of this model, made with fused quartz fibres 10 and 50 μm in diameter, gave excellent agreement between calculation and experiment, especially with perpendicular polarisation[42]. The advantage of using a model approach is clearly demonstrated in Refs.42 and 43, where a system of new, very strong i.r. bands at 1100–900 cm^{-1} (which are not found in transmission) is satisfactorily interpreted by using a somewhat more detailed model of close-packed quartz fibres 10 μm in diameter (see Fig.2). In the case of spherical particles the R coefficient must be calculated with allowance for the increase in the relative contribution to R with the number of steps when the sphere is divided into flat layers. These problems are highly relevant to the future application of MATR spectroscopy in studies of industrial adsorbents and catalysts, most of which are used in a powder or fibre form, and also in studies of polymer fibres.

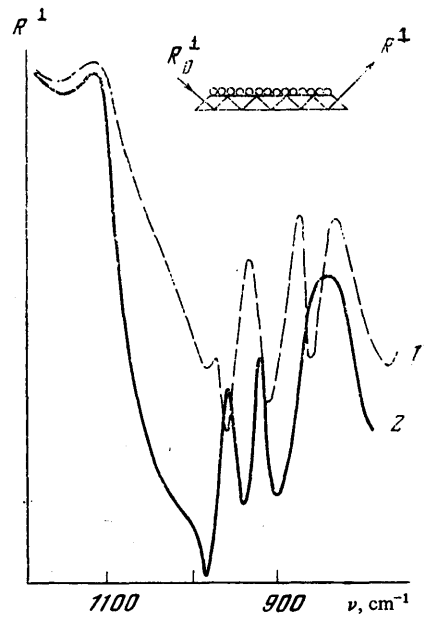


Figure 2. Comparison of experimental (*1*) and calculated (*2*) MATR spectra for close-packed quartz fibres 10 μm in diameter[43].

The roughness of surfaces with a fine finish has been studied[44] by using a model of the surface consisting of a system of intermediate layers with gradually varying values of n and κ. SiO_2 and LiF crystals were studied in the "residual ray" region. The optical properties of the transition

layer were modelled by the Lorentz–Lorenz equation in the complex form

$$\frac{\bar{n}_l^2-1}{\bar{n}_l^2+2}=\frac{\bar{n}_M^2-1}{\bar{n}_M^2+2}V+\frac{\bar{n}_s^2-1}{\bar{n}_s^2+2}(1-V),$$

where $\bar{n}_l$, $\bar{n}_s$, and $\bar{n}_M$ are the complex refractive indices of the layer of roughened surface, of the substance filling the uneven regions of the surface, and of the material M at a given depth within the sample respectively, and V is the proportion by volume of the bulk phase in the layer M. This approach has proved very successful in quantitative studies of the state of water and hydrocarbons adsorbed on micro-heterogeneous polished surfaces[29,45,46], and also in the study of microporous films[44,47–51].

2. Thin Films

Quantitative studies of thin films offer entirely new possibilities in the application of spectroscopic methods to practical problems in micro-electronics, integrated optics, and laser technology. However, allowance must be made for possible non-uniformities in very thin films, especially discontinuities in properties over the thickness of the film and roughness of the substrate surface, both of which can influence the optical properties of the film. The molecular adsorption of water on a polished fused quartz surface has been studied extensively[52–55], and the optical properties of the water film on an undulating surface with a small-scale roughness of 40–100 Å were shown to be markedly dependent on the optical characteristics of the substrate material and on the type of micro-roughness.

By allowing for these factors in the use of the Lorentz–Lorenz equation we conclude that the intrinsic spectroscopic properties of water in layers more than 10 Å thick (i.e. the shape and intensity of the stretching and bending vibration bands) are similar to those for ordinary liquid water. On the other hand, direct measurements of the refractive index of water in the very thin (~12 Å) gap between two flat surfaces in "optical contact" have revealed a clear dependence on the refractive indices of the two surfaces in contact.

A method of calculating the primary and the secondary structure of a polished surface has been developed from these these observations[45]. When the surfaces are brought in contact at a relative humidity of 50–60%, corresponding to an average thickness of 12 Å for the adsorbed water layer, the bending vibration at 1620 cm^{-1} shows a strong anomaly: its intensity is about 4 times greater than that of the corresponding band for liquid water[52]. As the relative humidity is increased the layer becomes thicker, and its optical properties become indistinguishable from those of liquid water at a thickness of 40 Å, but if the water layer is subsequently thinned the shape of the spectrum is unchanged (i.e. the spectrum does not revert to its initial state). Many hydrocarbon contaminants have been detected on these surfaces. The removal of these contaminants, which appear to be a residue from surface etching treatments, combined with special treatments to give hydrophilic surfaces, should enable thicker layers of water to be sorbed on the surface by a multimolecular mechanism. Comparison with ellipsometric measurements can be valuable, because very accurate thickness measurements on very thin films are possible by ellipsometry. The measurements suggest that the specific absorption of light by surface defects exceeds bulk absorption almost 100-fold[56].

Ellipsometry has been effectively combined with ATR spectroscopy in studies of the transition layer at the semiconductor–dielectric interface[57]. The adsorption of CO_2 on Si,[58] of H_2O on α-quartz[58], of proteins on polymers[59], and of proteins on carbon[60] have also been studied. As well as flat interfaces, layers adsorbed by porous systems have been examined by the ATR method[48–50,61].

3. Apparatus

A wide range of ATR and MATR attachments, mainly for the i.r. region, is now avaiable commercially. Apparatus for measurements in vacuum and at different temperatures is being developed[62,63], including the special MNPVO-3 MATR attachment which can be used with Soviet spectrophotometers (IKS-14, -22, -16, -29) as well as with the UR-20. This apparatus has already been used in a number of investigations, and has yielded very interesting results[29,43,45,52]. A vacuum adsorption cell is described also in Ref.64.

Attempts to develop a liquid-phase version of ATR spectroscopy resulted in the production of various attachments for the visible region[65]. Liquid MATR cells have been based on liquid chalcogenide glasses, especially As_xBr_yS, which are transparent in the i.r. region.[66–69] The standard ultra-high refractive index immersion liquids (with refractive indices up to $n = 2.1$) were shown[52] to have a set of wide transmission "windows" at 4000–750 cm^{-1}, making them suitable for use in ATR spectroscopy. Media with $n \geq 2.4$ have also been discovered.

Instrumental developments in ATR spectroscopy include, in addition to the construction of new attachments for the spectrophotometer, new designs of high-precision apparatus. These include the IRF-461 spectrophotorefractometer, developed for the simultaneous and accurate determination of both the optical constants n and κ of the complex refractive index[70]. Another recent development is the ISN-1, a multi-purpose industrial MATR spectrophotometer[71,72] which can be applied to a wide range of surface investigations.

The high sensitivity of the combination of MATR with Fourier spectrometers has allowed, for example, the measurement of MATR spectra in the i.r. region on polybutadiene filled with Aerosil and carbon black (up to 20 parts by weight per 100 parts of elastomer). The technique is particularly useful in studies of optically transparent electrodes, which attenuate the light beam up to 100-fold. Various problems in electrochemistry have been solved by using MATR cells coated with a film (up to 800 Å thick) of gold, platinum, or other conductor.

Plasma techniques have been used to clean the surface of ATR cells. Practical recommendations on the alignment of the apparatus and on corrections for a number of systematic errors (convergence of the light beam, uncertainty in the number of reflections, error in the angle of incidence) are made in Ref.11. Some of the recommended assemblies[11] have been used by other workers to determine n and κ for a number of liquids[73–79].

III. ADSORPTION

1. Surface Chemistry

The surface compounds which determine the selectivity of adsorbents and the catalytic properties of catalysts have been studied intensively by i.r. spectroscopy[80,81]. Whereas the transmission variant of i.r. spectroscopy is usually adequate for finely divided adsorbents and catalysts, having a large surface area, the MATR method has to be used to study the surface chemistry and the adsorption phenomena

of thin films supported on massive solids (silicon or germanium crystals, quartz, various glasses, crystals of halide salts, etc.)[82-84]. Special vacuum cells have been developed for MATR studies of surface compounds and adsorbed molecules[64,85].

The influence of surface treatment on the optical properties of the constituents of MATR cells has been studied in several laboratories. Surface treatment of a silicon MATR prism by hydrogen ions produces an absorption band at 2062 cm^{-1}, assigned to vibrations of the Si–H groups[86]. When silicon MATR elements are heated in water absorption bands due to amorphous silica appear at 1600–1850 cm^{-1}.[87] The MATR spectrum of thermally oxidised silicon includes absorption bands at 1870 and 1620 cm^{-1} (Si–O vibrations)[81]. Absorption bands from the OH group (3630–3650 cm^{-1}) and from the Si–H group (2250 cm^{-1}) are found in the spectrum of a silicon sample bombarded with phosphorus ions and heat treated in hydrogen[88]. Anodic oxidation of a silicon surface produces absorption bands from hydrogen-bonded hydroxyl groups in the MATR spectrum. Free hydroxyl and hydride groups have have been observed[89] on a silica surface heated at 1050° to 1200 °C in oxygen and water vapour. Molecular deposition reactions, in which the surface of a Si or Ge prism is treated with $SiCl_4$ or $GeCl_4$, produce strong bands at 1070 cm^{-1} (SiO_2) or 860 cm^{-1} (GeO_2, hexagonal) in the MATR spectrum[90-92].

MATR studies of porous silica films up to 1000 Å thick have yielded valuable information on the surface chemistry of this system. The films were prepared on the surface of MATR plates, and used as models of highly disperse adsorbates based on silica. One method of deposition used in this work was by electron-beam evaporation of crystalline silicon[47]. The initial spectrum of a film deposited on quartz by this method[85] included a broad absorption band at 3000–3700 cm^{-1}. Heating the sample to 50 °C produces bands at 3640 and 3460 cm^{-1}. When the temperature is raised to 150–200 °C the band at 3460 cm^{-1} is almost completely suppressed, and a band appears at 3670 cm^{-1}. After treating the sample in vacuum at 350–400 °C a band is observed at 3700 cm^{-1}, but the band at 3670 cm^{-1} does not disappear fully even after baking at 450 °C.[85]

Similar changes in the MATR spectrum have been reported for silica films deposited on silicon prisms[93] by the hydrolysis of $SiCl_4$ vapour at room temperature or from alcoholic solutions of $Si(OC_2H_5)_4$. Molecular water was found[93] to be almost completely removed by pumping at 35 °C. After dehydroxylation at 200 °C the spectrum shows an absorption band from hydrogen-bonded surface hydroxyl groups (at 3520 cm^{-1}) and a band from free hydroxyl groups on the micropore surfaces (at 3680 cm^{-1}). Only the absorption band for the free groups (at 3700 cm^{-1}) remains after vacuum treatment at 400 °C. The shift of this band by 50 cm^{-1} as compared with the free hydroxyl group band on Aerosil (3750 cm^{-1}) [81] is explained by perturbations of these groups through interactions with the oxygen atoms of the micropores.

A systematic study of hydrolysis reactions on the surface of quartz glass, and of their relevance to surface defects in glass and hence to the strength of glass, has been undertaken by the MATR method[94-100]. An absorption band at 3650 cm^{-1} and a weaker band at 3500–3550 cm^{-1} can be observed in the MATR spectrum of the surface layer of quartz glass. The absorption band due to adsorbed water molecules disappears after the prism is heated to 300 °C.[95] The influence of the thickness of the layer containing hydroxyl groups, and of the polarisation state of the light, on the precision with which the concentration of hydroxyl groups in quartz glass can be determined by the MATR method has been the object of a special study[96].

The hydrolysis of a quartz glass surface in a saturated aqueous solution of silica at 200–300 °C is discussed in Ref.97. The real strength of the glass (with surface defects) was found to increase with the temperature and the duration of the immersion in the aqueous solution. This effect is ascribed to preferential hydrolysis of the most highly stressed siloxane bonds on the surface of the glass. The strength of etched quartz glass has been shown to depend on the hydrolysis of a small proportion of the surface bonds[98]. The hydrolysis of quartz glass in an autoclave at 70–240 °C affects a surface layer 2–10 μm thick[99]. On the other hand, the nucleation and fast growth of all types of defect, accompanied by a large decrease in strength, occurs at the cristobalite (200–300 °C) and quartz (570–600 °C) phase transition temperatures of the crystalline modifications of silica[100].

The surface chemistry of other solids also has been studied. Thus, the MATR spectra of polished samples of gallium arsenide which had been stored in water show absorption bands at 700 cm^{-1} (Ga–O, As–O), 1550 cm^{-1} (Ga=O, As=O), and 850 cm^{-1} (Ga–OH, As–OH).[101]

MATR studies of the surface chemistry of powdered adsorbents deposited on a prism have been less successful, owing to the limited volume of material which can be irradiated. The MATR method has been used[102] to study the spectrum of surface hydroxyl groups in powdered α-quartz of 0.5 μm particle size. After heat treatment in vacuum at 200 °C the powder gave narrow symmetrical bands at 3649 and 3627 cm^{-1}, which were assigned to two different types of free hydroxyl group on the surface. The absorption bands from structural hydroxyl groups in zeolite (at 3740 cm^{-1}) were shown[103] to be much weaker in the MATR spectra than in transmission spectra.

The MATR method is very valuable in surface studies of carbon adsorbents, which end to absorb and scatter the i.r. radiation[104-107]. Thus, MATR spectroscopy has been used[104] to identify the functional groups on active carbon surfaces. The MATR spectra (at 1000–2000 cm^{-1}) of sugar charcoal activated in O_2 or $CO_2 + O_2$ atmospheres denote the presence of surface carbonyl and carboxyl groups[106]. Carbon films deposited in a vacuum on a KRS-5 element were investigated[107]: after being oxidised in a solution of $K_2S_2O_8$ these films gave absorption bands from CO groups (at 1710 and 1736 cm^{-1}) and bands from aliphatic CH groups (at 2850 and 2920 cm^{-1}).

The spectrum of a Cu film 20 Å thick deposited in a vacuum on a KRS-5 prism and subsequently exposed to the air showed absorption in the region of 700–320 cm^{-1}, consistent with the formation of Cu_2O.[107]

2. Adsorbed Molecules

MATR has been used as a very sensitive method of checking the freedom from organic contaminants of single-crystal silicon surfaces. The sensitivity of the detection of aliphatic organic compounds on the surface of a silicon element is 3×10^{-9} g cm^{-2}, and higher than the sensitivity of the methods of surface control used in the electronic components industry[108]. When the element has been washed in de-ionised water the MATR spectrum is found[109] to include absorption bands from the stretching vibrations of CH groups in aliphatic hydrocarbons present on the surface at a concentration of 3×10^{-8} g cm^{-2}. Heating the silicon plate in alcohol causes partial removal of the surface oxide layer, together with its associated organic contaminants[110,111].

The adsorption of stearic acid molecules on single-crystal surfaces has been studied in detail[112–116]. Sharke[112] examined the monolayers of stearic acid and its esters on germanium prism. The sensitivity of the detection, using the absorption bands of C–H and C=O stretching vibrations, was 2.3×10^{-7} g cm^{-2}. Dimeric molecules of the fatty acid are adsorbed preferentially from solutions of stearic acid in CCl_4 of 0.005–0.01% concentration[113]. The interaction between stearic acid molecules and a silicon surface is reported[113] to be significant only at solution concentrations >0.01%, though the effects become noticeable even at lower concentrations if the adsorbed water molecules are previously removed.

The MATR method[114] has been used to measure the adsorption isotherm of stearic acid from CCl_4 solution on the surface of a silicon prism (curve *2* of Fig.3). The result is compared with the Gibbs adsorption isotherm in curve *1* of Fig.3. The concentrations of adsorbed molecules were determined after removing the prism from the solution. The sensitivity of the detection of stearic acid on the prism from the 2920 cm^{-1} band was 3×10^{-9} g cm^{-2}. The portion of the isotherm near the first point of inflection (at low concentrations) corresponds to the surface area occupied by one molecule of stearic acid (154 Å), and is consistent with a planar orientation of the molecules along the prism surface. The region of almost constant surface concentrations, in equilibrium with concentrations of $2–3 \times 10^{-4}$ mole fraction, corresponds to a sloping portion of the Gibbs adsorption isotherm, for which the surface is covered with a monolayer of molecules oriented at an angle to the surface. The point of inflection (curve *1* of Fig.3) at an equilibrium concentration of 4×10^{-4} mole fraction corresponds to an area of 20.5 Å^2 per molecule, and therefore indicates molecular orientation at right angles to the surface in the close-packed monolayer. The MATR spectra of adsorbed stearic acid molecules measured at the points of inflection of the isotherm are consistent with a change in orientation of the molecules, from planar through sloping to vertical. These changes are accompanied by an increased contribution from the "crystalline" form of the adsorbed molecules.

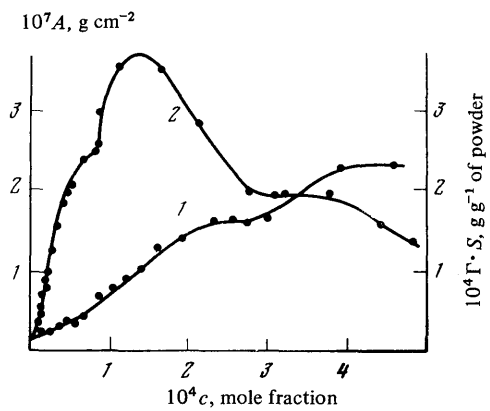


Figure 3. Adsorption isotherms for stearic acid on silicon: *1*) Gibbs adsorption (Γ) on powdered silicon from CCl_4 solutions; *2*) surface concentration of stearic acid (A) adsorbed on a silicon MATR prism from solution in CCl_4 (S is the surface area of the powder)[114].

Polarised MATR spectra give additional information on the orientation of adsorbed molecules. Takeneka and coworkers[116] studied the polarised MATR spectra of molecular layers of stearic acid deposited on the surface of a germanium prism by the Langmuir–Blodgett method. They concluded that these films consist of a system of monoclinic crystals, oriented with their C axis at an angle varying from 217° to 35° (depending on the number of layers) to the normal to the stearic acid–germanium interface. Preferential growth of these crystals takes place in the plane parallel to the stearic acid–germanium interface. The thickness of a monolayer is 23.8 Å.

The aggregation and the orientation of large flat molecules on the surface of MATR elements has been studied also by other workers[117,118].

The spectrum of a monolayer of ethyl octadecanoate molecules on the surface of a germanium prism includes an absorption band for free CO groups (1745 cm^{-1}), but not for hydrogen-bonded CO groups (1710 cm^{-1}).[103] This shows that hydrogen bonds are not formed between molecules in the adsorbed state. Reaction between the carbonyl groups and the Ge surface is observed after lengthy storage.

The polarised MATR spectra in the visible region for Methylene Blue adsorbed on a glass prism surface are discussed in Ref.117. Adsorption cuases a change in the relative intensity of the absorption from monomeric (600 nm) and dimeric (660 nm) molecules, as well as the appearance of a new absorption band at 740 nm. These spectral changes are ascribed to preferential adsorption of the dimeric form. The polarisation measurements indicate a parallel orientation of the adsorbed molecules.

Polarised MATR spectra have been used[118] to study the orientation of 1,1-diethyl-2,2-carbocyanine bromide molecules on silver chloride and glass surfaces. On a silver chloride surface these molecules are adsorbed as aggregates or micelles, in which the plane of the molecules is perpendicular to the surface. On the other hand, on a glass surface the adsorption is mainly molecular, or in small aggregates of the sandwich type. Under the latter conditions there is no preferential orientation of the molecules with respect to the surface.

Very interesting results have been obtained from MATR studies of adsorption on adsorbents and catalysts of industrial importance, and on models of these adsorbents. The state of the adsorbate has been characterised by MATR studies of these materials in the form of oxide films on the surface of the optical elements. The small thickness of the films (<1 μm) and, therefore, the low absorption and almost total lack of scattering of the i.r. radiation ensure that the adsorbate is detected with a high sensitivity[119]. The sensitivity of detection of adsorbed water by the MATR method (using the 1625 cm^{-1} band) is 0.03% of a monolayer[93].

The adsorption properties of films prepared on the surface of silicon elements by the hydrolysis of $SiCl_4$ vapour are determined by the microporous structure of the film[93]. These films can adsorb water molecules, but not ethanol molecules: in other words, their pore diameter is $<4.7 \times 10^{-4}$ μm. Silica films prepared from alcoholic solutions of $Si(OC_2H_5)_4$ have a looser structure.

The adsorption of water molecules by films which have been dehydroxylated at 400 °C causes hydroxylation of the micropore surface[93]. The absorption bands produced by the adsorption of water molecules correspond to bending vibrations of the dimeric molecules (at 1625 cm^{-1}) and to stretching vibrations of the OH group in the strong hydrogen bond region (3300 cm^{-1}, see Fig.4). This suggests the formation of two types of hydrogen bond by the adsorbed molecules: with the oxygen atoms of the surface hydroxyl groups and

with the oxygen atoms on the micropore surfaces. Heating the films in air (to 400 °C) does not lower the adsorption of water molecules, but sintering effects are produced by heating the porous films to 700 °C.[120]

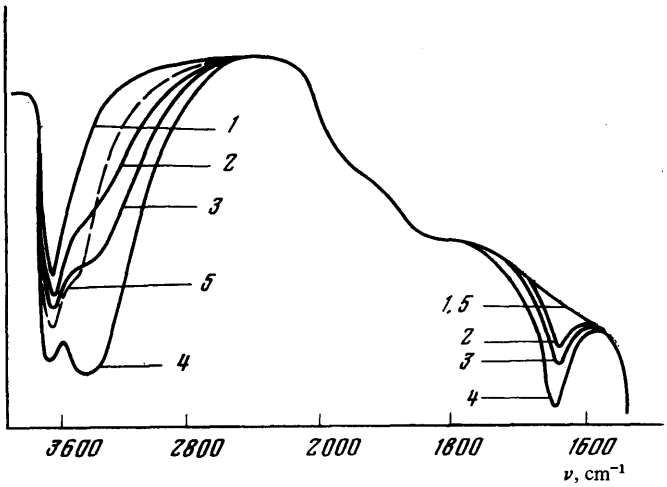


Figure 4. Infrared MATR spectra of water adsorbed on a silica film baked in vacuum at 400°: *1*) initial film, stored in vacuum at 30°, *2*) after adsorption of H_2O at 0.33 mmHg, 3) ditto at 0.8 mmHg, 4) after 4 days in contact with H_2O vapour at 0.8 mmHg, 5) after freezing out the H_2O vapour with liquid nitrogen[93].

The methods of quantitative evaluation of the MATR spectra (see II, 1) allow us to determine the amount of water adsorbed and to calculate the volume and diameter of pores in the film[47,62]. Absorption bands at 3650 and 3550 cm^{-1} were observed[47] in the MATR spectrum of SiO_2 films prepared by electron-beam evaporation in a vacuum and allowed to adsorb water from a moist atmosphere. The water content was determined from the intensity of the 3550 cm^{-1} band in films of different thickness prepared in different ways, and the pore volume was calculated in each case. An average pore diameter of 5–7 Å was obtained[47].

Changes in the MATR spectrum produced by the adsorption of $CHCl_3$ on films of this type heated to different temperatures indicate sintering effects at temperatures as low as 100 °C.[85]

MATR spectroscopy has been used[121] to determine the water content of thin films of SiO_2, MgF_2, and ZnS deposited by vacuum evaporation on Si, Ge, and KRS-5 prisms. The layers were shown to be fully saturated with water after admission of air at a relative humidity of 60–70% into the vacuum chamber. The changes in optical characteristics of the layer are throught to be due to the increased refractive index produced by the filling of the micropores by water molecules.

ZnS films prepared by laser evaporation in air have also been examined[51]. Their MATR spectra contained bands due to adsorbed water and hydrocarbon molecules.

The pore surfaces of films prepared by vacuum evaporation may contain, in addition to hydroxyl groups, other adsorption centres of the acceptor type which can induce major changes in the electronic structure of adsorbed molecules. Thus, anomalous band intensities as well as new absorption bands are observed[119] in the MATR spectra of $CHCl_3$ and CCl_4 molecules adsorbed on Ge and MgF_2 films evaporated in a vacuum by the electron beam method. Most of the water adsorbed on gallium arsenide layers was found[101] to be in a molecular form, attached to the surface by donor–acceptor bonds.

The MATR spectra of all the films obtained by vacuum deposition of SiO_2, ZrO_2, GeO_2, In_2O_3, Al_2O_3, NdO, MgF_2, SrF_2, NdF_2, CaF_2, ZnS, and Sb_2S_3 were found to contain an absorption band due to adsorbed water (3350 cm^{-1}). Various studies of the effect of deposition rate, residual gas pressure, and substrate temperature on the porosity of these films have been reported[62,122,123].

The MATR spectra of molecules adsorbed on single crystals of aluminium oxide are particularly interesting, because this compound is widely used as an adsorbent and a catalyst. The polarised MATR spectra of surface hydroxyl groups have been measured[124] on the (0001), (1123), and (4150) faces of an α-Al_2O_3 crystal. Molecular orientation in monolayers of calcium stearate and n-pentanol on the (4150) face was determined, and the adsorption isotherms were measured on all three faces at 30–120 °C. The isosteric heats of adsorption for a film 0.4 of a monolayer thick on the (0001), (1123), and (4150) faces were 13, 19, and 26 kcal $mole^{-1}$ respectively.

The MATR spectra of stearic acid molecules adsorbed from CCl_4 solutions on Ge and on Al_2O_3 (0001 face) prisms have been studied[115] with a Fourier spectrometer. The maximum detection sensitivity was 0.03 of a monolayer. The authors discuss in detail[115] the application of MATR spectroscopy to adsorption and desorption kinetics, adsorption isotherms, adsorbent–adsorbate interactions, molecular orientation, and to the structure and chemisorption of layers of adsorbed molecules.

The polarised spectra of CO molecules adsorbed on palladium salts deposited on the surface of a NaCl prism have been measured[125]. The low-frequency absorption bands (<1800 cm^{-1}) are assigned to CO molecules adsorbed with a high heat of adsorption (~40 kcal $mole^{-1}$) on Pd atoms from low-index crystallite faces, whereas the absorption bands at 1800–2000 cm^{-1} are associated with bridging structures found only on some of the faces of the Pd crystallites. Linear surface structures are found on Pd atoms of all the faces of the crystallites.

MATR spectra have been used[106,107,117] to study adsorption on opaque carbon films. The spectra of *p*-nitrophenol adsorbed on charcoal[106] and on carbon black[117] are consistent with the formation of donor–acceptor complexes with surface carbonyl groups. The spectra of albumin adsorbed on evapported carbon films have also been described[107].

The MATR method is also being applied to studies of biological materials, including bacteria[126]. A method of measuring the adsorption and desorption isotherms of water on protein films deposited from aqueous solutions on the surface of a KRS-5 prism has been described[127]. The MATR adsorption isotherms for water molecules on egg albumen and on tropomyosin were shown to be identical to those given by the MacBain balance.

The MATR method can be used also to study molecules on powdered adsorbents. Thus, it has been applied in the identification of compounds in chromatographic spots in the

separation of mixtures of *o*- and *p*-nitrotoluenes with 2,4-dinitrotoluene and of a mixture of *o*-, *m*-, and *p*-anisidine[128], and in the separation of steroids by thin-layer chromatography[129]. The MATR spectra of the dye Crystal Violet adsorbed on silica gel[130] and of ethyl xanthogenate on the surface of copper powder particles[131] have also been reported.

We should stress the need for the utmost caution in interpreting the spectra of adsorbed molecules near strong absorption bands due to the adsorbent[132], because bands from surface polaritons can appear in the MATR spectra of powders on the high-frequency wing of the adsorbent band (see II, 1).

IV. PHYSICAL CHEMISTRY OF POLYMER SURFACES

ATR spectroscopy has been applied very effectively to studies of polymeric materials, whose physical and mechanical properties are very well adapted to the technique. The possibilities of the method in studies of the surface layers of polymers have been demonstrated in several investigations[133–141].

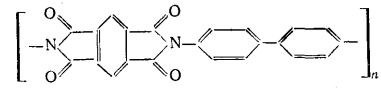
A series of papers[142–144] deals with the molecular mechanism of polymer degradation under mechanism load, and explains the role of surface layers in the degradation of polymers. The concentration of defects produced by the breakdown of macromolecules has been determined in low-pressure, intermediate-pressure, and high-pressure polyethylene (PE),[144] in rubbers and vulcanised products from natural and synthetic latex[142,143,145], and in poly(ethylene terephthalate) (PETP).[146] When the samples are subjected to mechanical load the concentration of end-groups in a surface layer 1 μm thick becomes 1–3 orders of magnitude greater than in the bulk (depending on conditions). Macroscopic cracks in the surface layer become saturated with decomposition products of the polymer molecules[143]. Using the shift of the vibration frequencies in the i.r. spectrum produced by mechanical loads, the stress in loaded PETP samples was shown to be as high as 700 kg mm^{-2}, i.e. close to the theoretical strength of the material[146]. The overloaded bonds are the first to break under the influence of thermal fluctuations, and therefore the enhanced concentration of these bonds in the surface layer (one order higher than in the bulk) explains the important role played by the surface layer in controlling the degradation of polymers under mechanical stress.

In ATR spectroscopy the absorption depends on the direction in which the radiation is polarised[5]. With anisotropic samples, the advantages of ATR measurements in polarised light over ordinary absorption spectroscopy include the possibility of studying strongly absorbing materials, the decoupling of the absorption coefficients for the three spatial directions (k_x, k_y, k_z),[147] and the possibility of studying the orientation of molecules on the surface independently of their orientation in the bulk.

Flournoy developed the theory of the interaction of a damped light wave under ATR conditions with an anisotropic medium[147], and he subsequently used it[148] to determine the orientation of macromolecules in uniaxially oriented films of polypropylene. Among the many investigations using polarised light one of the most noteworthy is a study[149–151] of the spontaneous orientation in planes of polypeptide and protein macromolecules in the α-form. Planar orientation was shown to occur mainly in a thin surface layer directly adjacent to the substrate, and to become gradually less pronounced with increasing distance from the substrate.

A study[52,153–156] of various polyimides has established the planar orientation of the macromolecules, brought about by cooperative effects involving the macromolecules in media bounded by a planar substrate. The techniques used in the analysis of ATR spectra of fibres (of organic or inorganic origin) are discussed in depth in Refs. 43 and 52. Polarised ATR spectroscopy and wide-angle X-ray diffraction have been used to show that the functional NH and C=O groups in aromatic polyamide fibres are oriented at right angles to the fibre drawing axis[157]. Shushkov and coworkers[158,159] studied the orientation of molecules in polyester fibres, and showed that under axial stretching PETP fibres undergo a transition from folded *gauche* conformations to stretched *trans* conformations. Oriented PETP fibres are discussed also in Refs. 160–162.

The angles between the moments for the vibrational transitions and the axis of the macromolecule have been calculated for several bands in the ATR i.r. spectra[52,154,155,162]. Satisfactory consistency between the spectroscopic results and X-ray diffraction data has been obtained by using the crystallinity bands. Oriented films of polytetrafluoroethylene have been studied by the MATR method using polarised light[163]. The more marked dichroism of the bands at 1150 and 553 cm^{-1} in the MATR spectra (as compared with the transmission spectra) was interpreted as evidence for a greater degree of orientation of the macromolecules in the surface layer than in the bulk. We have compared[164] the surface and the bulk properties of a polyimide film prepared from the dianhydride of pyromellitic acid and 4,4′-diaminophenylene:



By comparing the transmission and the MATR spectra in polarised light we also concluded that states of the macromolecules not found in the bulk are produced at the surface of samples by heat treatment.

The ATR method has been used to study the interaction between poly(dimethylsiloxane) (SKT) and a filler (Aerosil), and the observed spectral effects were explained by the formation of hydrogen bonds between the hydroxyl groups of Aerosil and the Si–O–Si groups of SKT.[165,166] At the same time the orientation of the macromolecules in a uniaxially stretched regular polymer was examined, and it was found that in *cis*-polybutadiene and polyisoprene the surface orientation of the macromolecules varies with time, the dichroic ratios of some of the bands reaching a maximum several days after mechanical treatment of the sample. The longer relaxation times of the surface layers were ascribed to the involvement of supermolecular structures in the rearrangement, in contrast to the bulk orientation effects which involve only segments of the macromolecules. The reorientation time of the supermolecular structures on the surface can be 10^4–10^5 times greater than the reorientation time of the segments in the bulk of a stretched vulcanisate[167]. The ATR method has been used to analyse artificial leather-cloth made from poly(vinyl chloride), polypropylene film, layered plastics, adhesive tapes, carbon-filled (up to 3% and 20% respectively) rubbers[20] and elastomers[168], cellulose fibres[169], and some thermally stable fibres[170].

An investigation of layers of lipids and proteins adsorbed at the water–air interface has been reported[171–173]. Monolayers and multilayers freshly deposited on a germanium MATR element by the Langmuir–Blodgett method (80 reflections) were found to have i.r. spectra similar to those of the corresponding melts. On the other hand adsorbed layers allowed to stand for 160 h on the MATR surface yield bands which are characteristic of the crystalline state. These conclusions are confirmed by electron micrographs of the layers[172]. In two-layer structures the hydrocarbon chains are oriented normal to the surface of the MATR element.

By varying the experimental conditions under which the ATR spectra are recorded (angle of incidence, relative refractive index n_{21}, state of polarisation of the light) the depth of penetration of the light and the effective sampling thickness can be varied between wide limits, thus extending the range of applications of the method to include diffusion problems. The idea was first formulated by Harrick[5], and realised experimentally by Carlsson and Wiles[174-176]. Photo-oxidation and treatment in a corona discharge of unstabilised polypropylene (PP) produces characteristic hydroxyl (3400 cm^{-1}) and carbonyl (1715 cm^{-1}) bands in both the transmission and the MATR spectra. Using a set of MATR elements made of germanium and of KRS-5 the authors[174-176] varied the relative depth of penetration d_p/λ from 0.066 to 0.201, and this allowed them to observe a gradual decrease in the relative optical densities D_{1715}/D_{2840} and D_{3400}/D_{2840} with increasing depth. The decrease in concentration of carbonyl and hydroxyl groups in a direction normal to the sample surface is approximately exponential.

Subsequently[177-181] the ATR method was used to study the oxidation of polyolefins by ozone by determining the concentration gradients of carbonyl oxidation products in polyethylene. Using a semi-cylindrical ATR element the effective thickness was varied over a wide range by varying the angle of incidence θ. If the sample contains a concentration gradient of more than one group the method gives the overall trend to a good approximation. Plots of $D_{C=O}/D_{C-H}$ against $d^{\perp}_{eff}$ (where $d^{\perp}_{eff}$ is the effective thickness of the layer for perpendicular polarisation of the light) are shown in Fig.5.

The following expression has been obtained[180,181] for the dependence of the concentration of carbonyl products on $d^{\perp}_{eff}$:

$$c_{C=O} = \frac{D_{C-H}}{\varepsilon_{C=O} d^{\perp}_{eff}} \cdot 10^{a/d^{\perp}_{eff}+b},$$

where D_{C-H} is the optical density of the band used as an internal standard, $\varepsilon_{C=O}$ is the molar absorption coefficient, and a and b are empirical constants. Differentiation of these curves with respect to $d^{\perp}_{eff}$ should give the concentration gradients of oxidised groups in depth. As Fig.5*b* shows, most of the carbonyl products of the oxidation of polyethylene by ozone are concentrated in a surface layer a few micrometres thick.

Quantitative tests of the validity of Fick's law in polymer diffusion are conveniently carried out by this approach. The diffusion coefficients of methanol and acetone in polyisobutylene rubber have been measured[182] by the single ATR method. Two thermal diffusion schemes, shown in Fig.6, were used in this experiment. In the scheme of Fig.6*a* the surface *AA'* of the rubber film is in intimate (adhesion) contact with the surface of the ATR element, and its other surface is in contact with the diffusant. In this case the penetration of the diffusant is monitored from the increase in the

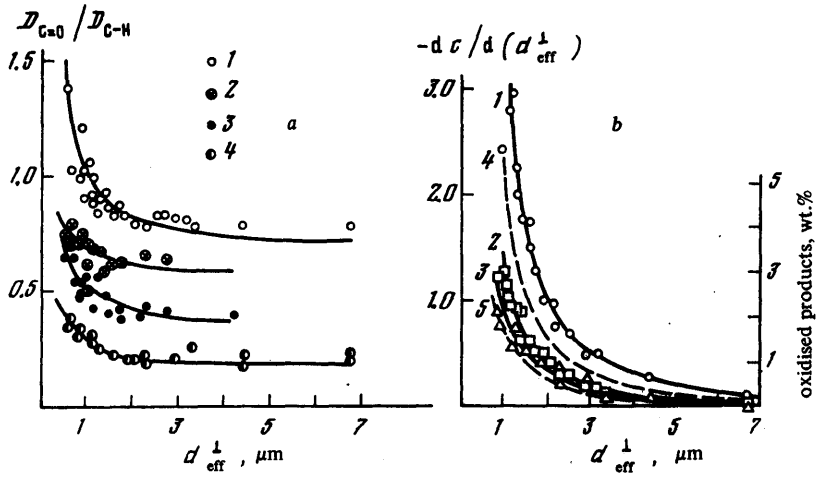


Figure 5. (*a*) Relative optical density $D_{C=O}/D_{C-H}$ against $d^{\perp}_{eff}$ for polyethylene (*1*, *2*) and polypropylene (*3*, *4*) oxidised by ozone: *1*) 170 mg $litre^{-1}$ of ozone, oxidation time 5 h; *2*) 170 mg $litre^{-1}$ of ozone, oxidation time 1 h; *3*) 130 mg $litre^{-1}$ of ozone, 5 h; *4*) 130 mg $litre^{-1}$ of ozone, 1 h. (*b*) plots of $dc/d(d^{\perp}_{eff})$ against $d^{\perp}_{eff}$ for polyethylene oxidised by ozone (170 mg $litre^{-1}$) for different times (*1*) 5, *2*) 1, *3*) 0.5 h), and variation with depth of the concentration of oxidised groups in polyethylene oxidised with ozone (170 mg $litre^{-1}$) for different times (*4*) 5, *5*) 1 h).[181]

relative optical density of the analytical band. In the second scheme (Fig.6*b*) the surface *BB'* (which had been in direct contact with the diffusant) is pressed against the ATR element. The concentration gradients of the diffusant as a function of the film thickness *l* measured in this way are shown in Fig.6c for different times t_n. The equation obtained [182] accurately describes the kinetics of the changes in diffusant concentration in the polymer in the direction of d_p and at time *t*.

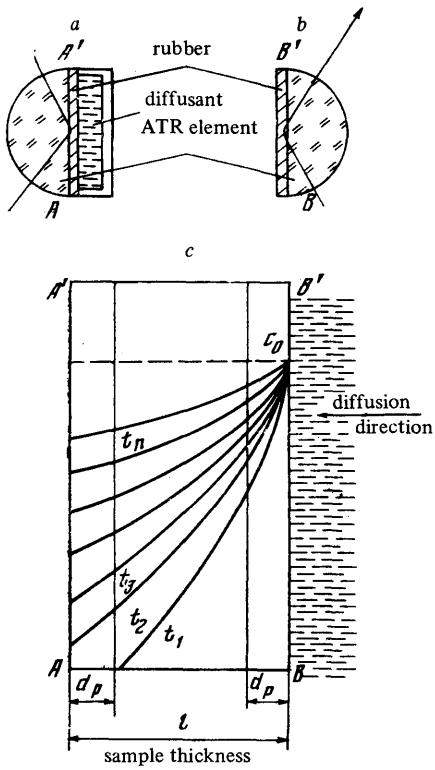


Figure 6. Two arrangements of the diffusion experiment in rubber. (*a*) diffusion monitored from the *AA'* surface; (*b*) diffusion monitored from the *BB'* surface, which had previously been in contact with the diffusant; (c) is a schematic presentation of the concentration profile of diffusant through the thickness of the rubber film at different times (t_1, t_2, ... t_n); c_0 is the concentration of diffusant at the surface; the depth of penetration of the radiation is given[182] as $d_p = \lambda_1/2\pi(\sin^2\theta - n_{21}^2)^{1/2}$.

A similar experimental arrangement was used[183,184] to study the diffusion kinetics of non-solvents in elastomers by the MATR method. This approach confirmed[185] the authors' previous suggestion that the surface layer of a polymer in adhesional contact with a solid surface has an abnormally high density. During diffusion, or heat treatment, the macromolecules undergo transitions into more probable conformations, giving a more uniform density distribution.

The diffusion coefficients of ethyl acetate in polyethylene and of ethanol in poly(butyl methacrylate) have been measured[186,187] by applying Fick's equation to the ATR results. By varying the reflection conditions a decrease in the concentration of epoxy resin with increasing distance from the resin–polysiloxane rubber interface was detected[188].

Since the oxidative degradation of polymers often begins at the surface, internal reflection spectroscopy can give important information on the initial steps of the processes involved.

Measurements of the optical density ratio of the bands at 720 and 730 cm^{-1} in the MATR spectra of PE which had been exposed to ozone revealed[189,190] an increase in the degree of crystallinity, arising from the preferential "combustion" of the amorphous phase[191]. By combining ATR measurements with electron microscopy and low-angle light diffraction it was established that in linear polyethylene the supermolecular formations in a surface layer ~1 μm thick are the same as those in the bulk. However, there are large differences in internal structure between the bulk and the surface: the crystallite orientations are different, and the amorphous regions of the surface layer contain an abnormally high proportion of folded molecules with a large number of defects. The main difference between the surface layer and the bulk lies in the structure of the molecules in the amorphous regions[152]. It has also been shown, by the MATR method, that previously unknown but stable hydroxy-, keto-, and alkoxy-acids with a very low content of C–H bonds can be produced by deep oxidation of PE with ozone[189].

The mechanism of the oxidative degradation of PE at the copper–PE interface is discussed in Refs.192 and 193. It is shown that the formation of carbonyl-containing products is markedly accelerated at a surface in contact with copper, and that the MATR spectrum of the copper surface contains bands suggesting the formation of carboxylic acid salts which act as catalysts for the oxidation of the PE.

Accelerated photo-oxidation of PE in the presence of titanium dioxide[194], and the effect of thermal and oxidative degradation on the adhesion of PE to aluminium[195,196], have been reported. The dependence of adhesion on the time of heat treatment goes through two maxima, which are explained by postulating simultaneous oxidation and structural rearrangement processes in the surface layer of PE. Experiments on the adhesion of PE to a quartz MATR element led to the hypothesis that hydrogen bonds can be formed between functional groups on the PE surface and the surface hydroxyl groups of the quartz[197].

Under practical conditions the surfaces of many materials are exposed to corona discharges, and therefore particular attention has been devoted to this type of interaction. For example, polytetrafluoroethylene has been exposed to air and to ammonia under corona discharge conditions[22]. In the air atmosphere volatile degradation products are formed, and desorbed from the PE surface, whereas in the ammonia atmosphere surface modification occurs to a depth of several micrometres. Extensive investigations of the effect of corona discharges on polyolefin surfaces have been reported[174–176]. The infrared ATR spectra of polyamide films which had been exposed to a glow discharge showed intensity changes in the stretching vibration bands of the C–H groups and in the Amide II bands (1550 cm^{-1}), and an increase in the concentration of carbon products[198].

In conclusion we should mention a short review of the application of ATR to studies of polymers and fibres[199], and a useful applied investigation of adhesive tapes in which the effect of the position, size, and shape of the polymer sample on the quality of the MATR i.r. spectra is clearly brought out[200].

V. ELECTROCHEMISTRY

Electrochemists have always been concerned with structural changes on electrode surfaces and in the layer of solution in contact with the electrode, but until recently direct (and non-destructive) methods of observation were not available. Adsorption and reflectance spectrophotometry and ellipsometric methods are now being applied in electrochemistry. A discussion of the whole range of optical methods lies beyond the scope of the present review, and interested readers are referred to recent publications on this topic[201-203]. Some of the most recent work has dealt with an experimental arrangement called the optically transparent electrode (OTE) in the English and American literature, which can be set up by using conventional absorption spectrophotometry[203-205] or ATR spectroscopy[206]. We shall confine our discussion to the OTE relying on internal reflection.

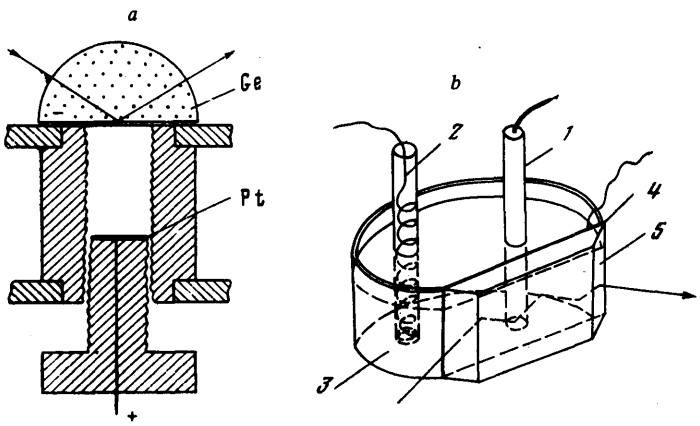


Figure 7. OTE cells based on (*a*) ATR [187] and (*b*) MATR [201] elements: *1*) calomel reference electrode, *2*) external gold electrode, *3*) electrolyte solution, *4*) gold OTE, *5*) glass MATR element.

Ordinary single or multiple reflection elements are used as OTEs in the ATR mode by coating their surface with a thin (200–800 Å) conducting layer of tin oxide, gold, platinum, or carbon. Different types of OTE are described in Ref.12; two examples are shown in Fig.7. These ATR cells are placed in the cell compartment of the spectrophotometer, and the i.r. or u.v. spectra are recorded during the electrochemical experiment. The thin layer of conductor on the surface of the ATR element does not prevent the penetration of light into the electrolyte solution, but it attenuates it very strongly, and therefore the theory of ATR with allowance for thin films and multi-layer coatings must be used in the quantitative evaluation of the results[14,201]. Fig.8 shows the u.v. ATR spectra of a solution of the dye Eosin Y, obtained with an ordinary glass MATR element and with a gold-coated element respectively[201]. The enhanced intensity of the bands in the case of parallel (as opposed to perpendicular) polarisation of the light is consistent with the theory developed by Hansen[16].

The use of MATR elements coated with conducting films introduces complications into the spectral analysis owing to the possibility of resonance effects[207]. Some workers prefer to use uncoated germanium elements (for the i.r. region). Operation in the visible region of the spectrum is thought[201, 206] to offer some advantages: firstly, because electrolytes are usually transparent in this region, and secondly, because effective thicknesses are small and therefore thinner films can be studied, even in the region of light absorption by the electrolyte. The optimum film thickness can be calculated if the optical constants of the medium for the relevant spectral region are known.

In the visible region the depth of penetration of the radiation into the optically less dense medium is ~50 nm. If a compound having a diffusion coefficient of 10^{-5} cm^2 s^{-1} is formed on the OTE surface during the electrochemical process, a concentration gradient falling by 1% at a depth of 400 nm will appear within 1 s. At that depth the amplitude of oscillation of the electric vector of the electromagnetic field is damped to one thousandth of its value at the surface. Thus, rapidly plotted ATR spectra can give valuable information on surface concentration in the case of electrochemical effects on OTEs with time constants of the order of 1 s.

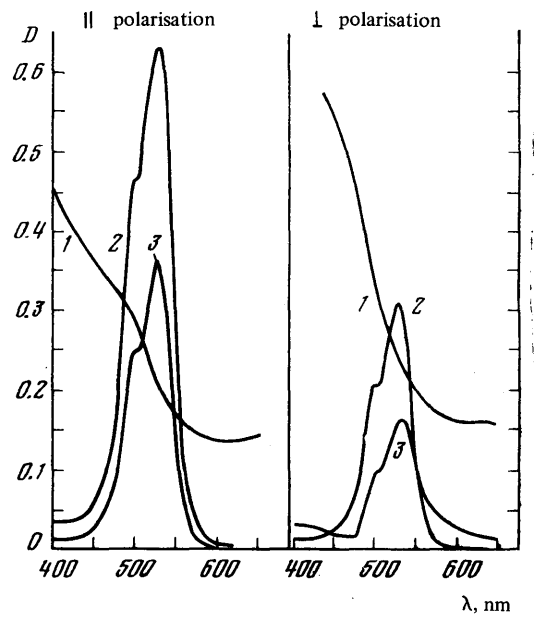
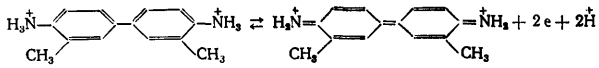


Figure 8. Internal reflection spectra of solutions of the dye Eosin Y: [201] *1*) reflectance spectrum of the gold OTE; *2*) Eosin Y on the gold OTE; *3*) Eosin Y on the glass MATR element.

As an example of this type of problem we may consider one of the earliest OTE investigations[208]: a study of the electrochemical oxidation of o-toluidine in hydrochloric acid. A glass plate coated with a film of SnO_2 was used as the MATR

element. The depth of penetratration was ~60 nm. The electrochemical reaction



involved the two-electron oxidation of *o*-dimethyl-*p*-phenylenediamine on the electrode surface with formation of an intermediate product with an absorption band at $\lambda_{max} = 438$ nm. From the time dependence of the optical density D_{438} and of the electrode potential the concentration and the extinction of this compound were calculated, as well as the rate constant of its disproportionation reaction.

An important experimental paper[209] suggests the use of OTEs in quantitative studies of processes as a function of distance from the electrode surface, and considers the electrochemical oxidation of *p*-anisylamine as an example.

OTEs have been used to study a wide range of electrochemical reactions, including the electrochemical behaviour of lithium perchlorate in dimethylsulphoxide on a germanium surface[210], the anodic oxidation of potassium ethyl xanthate in water (by measuring ATR spectra at different values of the anode potential)[211], and the kinetics of the disproportionation of zinc tetraphenylporphyrinate[212]. Among the most important applied investigations is a study[213] of the electrochemical corrosion of germanium in sea water.

Most of the work to which we have referred is aimed at developing applications of the method to specific problems, and it represents a considerable step forward in this direction. However, systematic studies of electrochemical problems exploiting the OTE are far less numerous. One of the best known examples is the work of Trifonov and coworkers, who in 1970 described an ATR apparatus for studying electrochemically induced polymerisation on the surface of a germanium ATR element coated with gold[214]. The apparatus was applied to an investigation of the polymerisation of acrylonitrile induced by electrochemically generated radical anions[214–218]. Most of the measurements were made on the stretching vibration band of the C≡N group. The ATR spectra recorded[215,216] at various stages during the reaction are shown in Fig. 9. Intensity changes of some other bands were also recorded.

As a result of the kinetic study the following scheme was proposed for the cathodic reaction:

$$CH_2{=}CHCN + 2e \rightarrow [CH_2{=}CHCN]^{2-}.$$

Disproportionation of the anion causes the formation of a radical anion:

$$[CH{=}CHCN]^{2-} + CH_2{=}CHCN \rightarrow 2\,[CH{=}CHCN]^{\cdot-}.$$

Recombination of the radical anion produces a di-anion with an extended carbon chain:

$$2\,[CH_2{=}CHCN]^{\cdot-} \rightarrow [CNCH(CH_2)_2CHCN]^{2-}.$$

More recently the method has been used to study the polymerisation of 1-vinylimidazole[219].

Adsorption from solutions is another area of electrochemical research in which ATR techniques are being increasingly applied. Higashigama and Takenaka[220] exposed an electrochemical cell with a germanium electrode to polarised radiation, and they showed that for certain concentrations of sodium laurate in water the adsorbed layer of lauric acid on the OTE surface consists of uniaxially oriented crystallites,

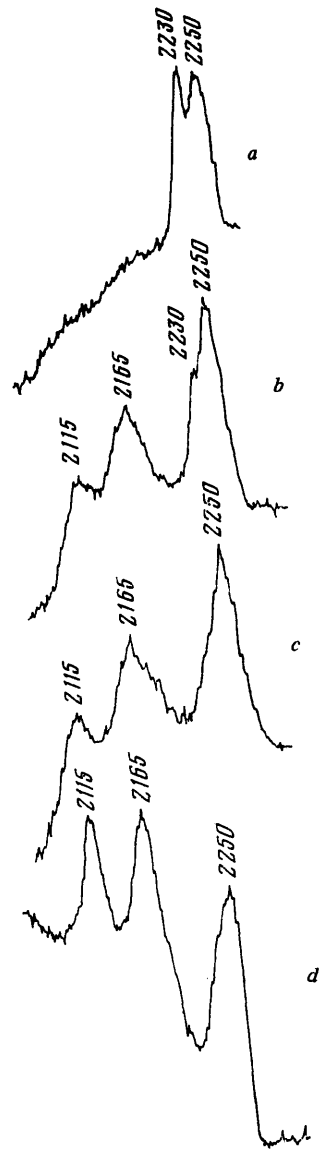


Figure 9. ATR spectra in the stretching vibration region of the C≡N group during electrolysis of acrylonitrile: (*a*) partially polymerised monomer (2230 cm^{-1}, monomer; 2250 cm^{-1}, polymer); (*b*) and (*c*) sequentially recorded spectra showing the appearance of the radical anion (2165 cm^{-1}) and of the radical dianion (2115 cm^{-1}); (*d*) spectrum for the highest achievable concentration of active particles[215].

with their crystal axis inclined at 39° to the normal to the electrode surface. When a critical concentration of sodium laurate is exceeded the adsorption becomes micellar. The effects of potential, pH, and temperature on the adsorption were also studied by the same method.

Two interesting papers[221,222] demonstrate the possibilities of modern infrared techniques. A carbon film 220–300 Å thick was evaporated on a germanium electrode. The transmission of this OTE at 1800 cm^{-1} was only 1.5%, but by using multiple scanning and scale expansion techniques it was possible to study the electrochemical adsorption of fibrinogen on the carbon electrode. The thickness of the adsorbed layer of fibrinogen was shown to be 250–350 Å. Two Amide I bands (1644 and 1614 cm^{-1}) and two Amide II bands (1553 and 1520 cm^{-1}) were observed at a surface potential of +150 mV. It was concluded that after electrochemically induced adsorption the fibrinogen molecules are present in two forms, one of which is stressed and relaxes to the normal form when the potential is removed.

The electrochemical adsorption of Methylene Blue from buffered solutions was studied in the u.v. region[223]; various examples of electrochemical reactions and adsorption on OTE surfaces are discussed in Ref.224.

Optical internal reflection spectroscopy has become one of the basic techniques of research on the physical chemistry of surfaces. The development of experimental techniques has advanced to the point where quantitative measurements can be justified. The topic most urgently in need of further theoretical development is the quantitative analysis of disperse systems by the ATR method.

The procedures so far developed can be used to analyse systems quantitatively in terms of both the optical constants over a wide region of the spectrum. This is important from the standpoint of measurement techniques, and also because it allows new problems to be formulated in surface physical chemistry. Current trends include combining the ATR method with other methods of surface investigation, such as Fourier transform spectroscopy. Internal reflection spectroscopy offers new perspectives in the study of the aggregation and orientation of molecules adsorbed on various surfaces, and important developments can be expected also in this direction.

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Papers published while the present review was in preparation include general discussions of a number of experimental problems in ATR spectroscopy[225–230], and a discussion of a correction for the quality of the contact between the ATR element and the sample[231]. Theoretical models have been used to derive expressions for the concentration gradients in surface layers[232–234], and to compare the surface and the bulk properties of glasses[235], polymer films, and fibres[236–241]. Recently reported studies deal with the influence of surface defects on the strength of polyamide fibres[242], the influence of electrical polarisation on the spectra of polyacrylonitrile[243], and the interactions of ozone with rubber[244] and polypropylene[245] and of a glow discharge with various polymers[246]. The work on the deposition of adsorbed layers of proteins on the surface of MATR elements by the Langmuir–Blodgett method has continued[247–250]. The adsorption of proteins on polyethylene[251], the diffusion of CCl_4 in Teflon[252] and of water in lipid layers[253], processes in photographic gelatin layers[254], and the photo-oxidation of dyes on an optically transparent ZnO electrode[255] have been investigated. New optical media for ATR have been developed[256–259], and industrial spectrophotometers[260–263] and associated equipment[264–267] have been put on the market. The ATR method has been used in Raman spectral studies[268–270], and in various problems in materials science[271], in geochemistry and petroleum chemistry[272–274], and in the protection of the environment[266,275,276].

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