

Infrared External Reflection Spectroscopy of Adsorbed Monolayers in a Region of Strong Absorption of Substrate

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There are a number of systems in which the substrate shows a spectral strong absorption in the region of the characteristic vibration of the surface species. These systems are extremely difficult to study because of the overlapping of a small spectroscopic signal from surface species with a very strong absorption signal from the substrate. For example, major mineral components of hard tissue, carbonates and phosphates, show very strong absorbance in a relatively wide spectral region in which the characteristic vibrations of the carboxylate, amide, C–O, or other groups of soft tissue, having a biological importance, take place. The system chosen for the study was calcite with very strong absorption between 1600 and 1400 cm^{-1} due to carbonate vibrations and oleate which forms a calcium oleate surface complex with characteristic carboxylate absorbance bands at about 1500 cm^{-1} . It is shown, for the first time, that the experimental spectra of the oleate adsorbed species can be recorded successfully, at different incidence angles and two polarizations, in the spectral region of very strong substrate absorption. Moreover, the experimental spectra can be reproduced by spectral simulations, giving detailed information about the surface composition and structure of the produced adsorbed layers even for those with lateral heterogeneous structure. The adsorbed oleate forms surface calcium carboxylate species with two preferential conformations: unidentate-like (a band at 1537 cm^{-1}) and bidentate-like (a band at 1575 cm^{-1}). At multilayer coverage, the adsorbed layer forms a patchlike structure produced by a pillar growth mechanism. This spectroscopic structural finding was supported by atomic force microscope measurements. The various experimental and theoretical aspects of the infrared external reflection technique within a very strong absorbing region of substrate are also discussed. For comparison, a discussion of the aliphatic stretching vibration region in the recorded spectra, at about 3000 cm^{-1} , in which calcite is transparent is also performed.

Introduction

During the past almost 4 decades, infrared external reflection spectroscopy has been used extensively to examine the composition and structure of thin films deposited on metals.¹ With all metallic substrates, which are characterized by a high refractive index and absorption coefficient, the reflection spectra are recorded practically at the same grazing incident angle, which ensures the maximum sensitivity. The reflection spectra are easy to interpret by simple comparison with transmission spectra. This is a consequence of the presence, at a metallic substrate, of practically only one strong, vertical electric field vector which can interact with the adsorbed species. This is well-known as the surface selection rule.

For nonmetallic substrates with a low refractive index and absorption coefficient, the situation is more complex. The low reflectivity and strong dependence of the recorded spectra on the angle of the incident beam and polarization are very different for each substrate (optical effects) and cause some difficulties in properly carrying out the detailed surface characterization of these systems. The experimental problems related to these phenomena were overcome only quite recently. The full advantages of the infrared reflection technique in the case of nonmetallic substrates has been demonstrated lately in several papers,^{2–13} although the basic reflection theory for a stratified system on any type of substrate was developed about 3 decades

ago.^{14,15} To take full advantage of this technique virtually every system under investigation with a nonmetallic substrate should be theoretically considered using the spectral simulation procedure. This is vitally important from two points of view: (i) the correct interpretation of the recorded spectra, which are strongly modified by optical effects, and (ii) the optimization of the experimental conditions to record the most informative spectra with a high signal-to-noise ratio. At nonmetallic substrates, there are three electric field vector components which can interact with surface species. By proper manipulation of polarization and angle of the incident beam, it is possible to record a few spectra which together carry out a full 3D-like picture of the adsorbed species.

Hitherto, the majority of the investigated systems were limited to the systems with a one component adsorption layer and to the nonabsorbing region of substrate. A multicomponent adsorption layer does not pose a significant problem for its detailed characterization, as was shown in recent studies.¹¹ There are two works^{8,16} where the study of the surface species on nonmetallic substrates showing medium absorbance outside the spectral region of absorbance of surface species was recently reported. They showed clearly that at certain experimental conditions absorbance bands from the substrate (positive for s-polarization) can be easily differentiated from the absorbance bands of the adsorbed species (negative for s-polarization). This finding allows the absorbance bands due to different phases of the multiphase system to be distinguished and is very helpful

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to correctly assign the observed vibrations to particular molecular groups in complex systems.

There are numerous systems in which the substrate shows a strong absorption in the region of the characteristic vibration of the surface species. The very strong absorbance of substrate obscures low-intensity absorbance bands from surface species, making the systems extremely difficult to study spectroscopically at monolayer coverage. This situation occurs for many biochemically important systems such as major mineral components of hard tissue, carbonates and phosphates, which show very strong absorbance in a relatively wide spectral region in which vibration of carboxylate, C–O, amide, or other most characteristic molecular groups of soft tissue take place. The monitoring of biochemically important systems might be a new exploration area for the infrared external reflection technique.

In this paper, various experimental and theoretical aspects of the infrared external reflection technique within a very strong absorbance region of substrate are discussed. The interaction of calcite, with a very strong absorption between 1600 and 1400 cm^{-1} due to carbonate vibrations, with oleate, which forms a calcium oleate surface complex with the carboxylate group showing absorbance at about 1500 cm^{-1} , is described. The parameters which determine the spectral sensitivity and the position, intensity, and shape of the absorbance bands in the reflection spectra are discussed in detail. The result obtained demonstrate a unique advantage of external reflection infrared spectroscopy over other infrared techniques to acquire detailed information on a molecular level on interface interaction in various systems including the most complex such as biological systems.

Experimental Section

Materials. The natural mineral samples of calcite (Wards, Mexico) with dimensions of about $10 \times 20 \text{ mm}^2$ with an external surface obtained by cleavage were used in this study. X-ray diffraction confirmed the crystalline structure of calcite CaCO_3 with the (1014) surface orientation for a cleaved sample. In the adsorption experiments, only cleaved samples with exactly the same cleaved plane were used. The samples were cleaved instantly before contact with oleate solutions. Calcite was a very high purity transparent crystal.

More than 98% pure sodium oleate (*cis*-9-octadecenoic acid salt), supplied by Aldrich-Chemie, was used. Other reagents were all of an analytical grade. Distilled water from the Millipore (Milli-Qplus) system was used throughout the experiments.

Adsorption Studies. The calcite samples with a surface prepared by cleavage were instantly immersed, without any additional treatment, in 200 mL of oleate solution at $\text{pH } 10.0 \pm 0.2$ for a period of 1 min to 20 h. The oleate concentration was $3.3 \times 10^{-5} \text{ M}$. Immediately after contact with oleate solution, the samples were immersed in water at $\text{pH } 10$ for about 1 s and placed instantly in an FTIR spectrophotometer to record the reflection spectra. This procedure was applied in order to avoid deposition of oleate molecules from the thin film of solution remaining after the emersion of the sample from the adsorption solution.

Infrared Analysis. The infrared reflection spectra of slab samples were measured on a Bruker IFS55 FTIR spectrometer equipped with an MCT or DTGS detector and a reflection attachment (Seegull). A wire-grid polarizer was placed before the sample and provided p- or s-polarized light. These accessories were from Harrick Scientific Co. The reflection spectra of the adsorption layers were obtained by the use of polarized light and different angles of incidence. Other details of

experimental procedure could be found in our recent papers.⁸ The unit of intensity was defined as $-\log(R/R_0)$, where R_0 and R are the reflectivities of the systems without and with the investigated medium, respectively.

Results and Discussion

Optical Considerations. The recent instrumental development of infrared spectroscopy is contributing significantly to the increasing emphasis being placed on a molecular level (monolayer and submonolayer coverages) surface characterization. To push the sensitivity limit even lower and to perform the proper interpretation of reflection spectra for a more detailed picture of the interfacial structure, it is vitally important to combine such spectroscopic measurements with a spectral simulation technique. The importance of such combination is reinforced by the anticipated sensitivity of surface infrared absorbance not only to surface concentration but also to adsorbate structure, molecular orientation, chain conformation, and so-called optical effects. As a consequence, the band intensities and positions do not display any simple relationship with the surface composition. Therefore, the acquisition of quantitative surface compositional and structural information necessitates a carefully designed experimental procedure. It was discussed in detail in recent papers.^{5–13} The theoretical and experimental results show clearly that the optical consideration of the systems under investigation via simulation of various parameters provides an excellent basis for the detailed explanation of the recorded reflection spectra, as well as for optimization of the experimental conditions.

Determination of Optical Constants of Mineral Samples.

The optical properties of calcite in the infrared region are summarized by White.¹⁷ There are two very strong bands in the mid-infrared region which are due to the internal modes of the CO_3^{2-} ion and assigned to two active ν_2 and ν_3 vibrations at about 900 and 1400–1600 cm^{-1} , respectively (Figure 1). The latter vibration shows a very broad band which results from a very large splitting of the transverse and longitudinal components of the vibration. The magnitude of the splitting is related to the absorption strength which is very high for this vibration. The substrate absorbance makes it very difficult to monitor any characteristic bands of the adsorbed species in this frequency region. For example, the low-intensity absorption bands of the carboxylate group of the adsorbed oleate monolayers, which appear at about 1550 cm^{-1} , are very difficult to observe in transmission or diffuse reflectance spectra even if a substrate subtraction procedure is applied.

The stretching vibration band ν_3 at about 1450 cm^{-1} has a dipole moment perpendicular to the *c* axis of the rhombohedral unit cell (Figure 2); hence, it is possible to avoid the strong absorbance and to perform a characterization of the adsorbed species by the preparation of the calcite sample with an external surface parallel to the *c* axis and to use light polarized parallel to the *c* axis. In these conditions the very strong absorbance bands of the CO_3^{2-} ions in the 1400–1600 cm^{-1} region disappear, and recorded spectra will be free of the strong absorption band of the substrate. Although this solution seems to be very attractive, there are two disadvantages: (i) the sample surface prepared in this way is not a natural cleavage plane of calcite and (ii) the surface characterization of the adsorbed layer is limited to the electric field vector parallel to calcite interface (s-polarization). Because our aim is to study the interaction of oleate with a natural (cleavage plane) surface of calcite in detail (which requires employing also p-polarization mode) this solution was abandoned. The cleavage rhombohedron cell is

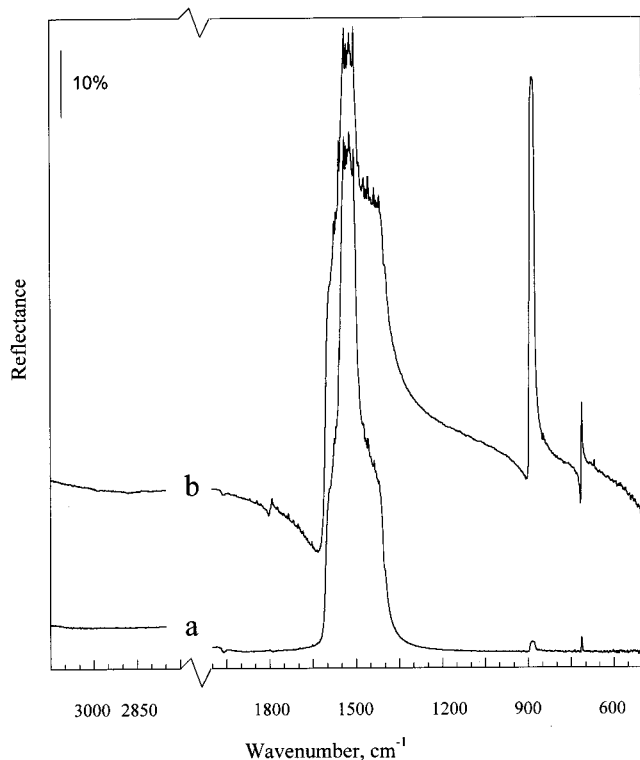


Figure 1. Reflection spectra of cleaved calcite sample recorded for (a) p- and (b) s-polarizations at an angle of the incident beam of 60° . The reference spectrum was aluminum mirror; the DTGS detector was used in the experiment.

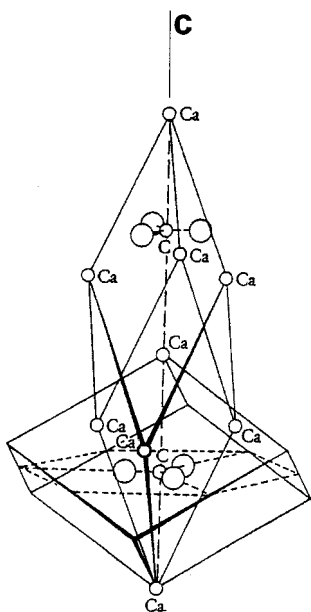


Figure 2. True rhombohedral unit cell ($Z = 2$) and the cleavage rhombohedron cell with position of Ca and CO_3 groups shown (after ref 18).

inclined to the c axis of the true rhombohedral unit cell as shown in Figure 2. This causes the spectra of adsorbed molecules on the cleavage plane recorded by external reflection techniques to show the strong and broad absorbance band in the $1400\text{--}1550\text{ cm}^{-1}$ frequency region (Figure 1).

This discussion also shows that the position of the calcite sample versus the incident infrared beam has to be the same during the recording of all spectra: (i) the spectra needed to determine optical constants, (ii) the background spectra of calcite before adsorption (R_0), and (iii) the spectra of the sample after

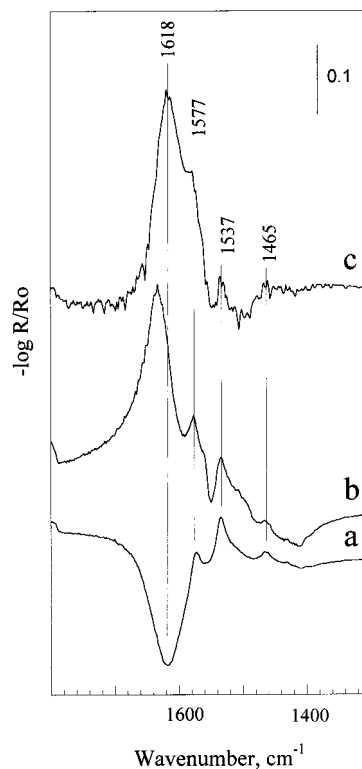


Figure 3. Reflection spectra of calcite after adsorption of oleate recorded at different conditions: (a) exactly the same positions of calcite before and after adsorption; (b) sample after adsorption turned 180° around axis vertical to surface plane versus sample before adsorption; (c) position of sample after adsorption turned about 8° .

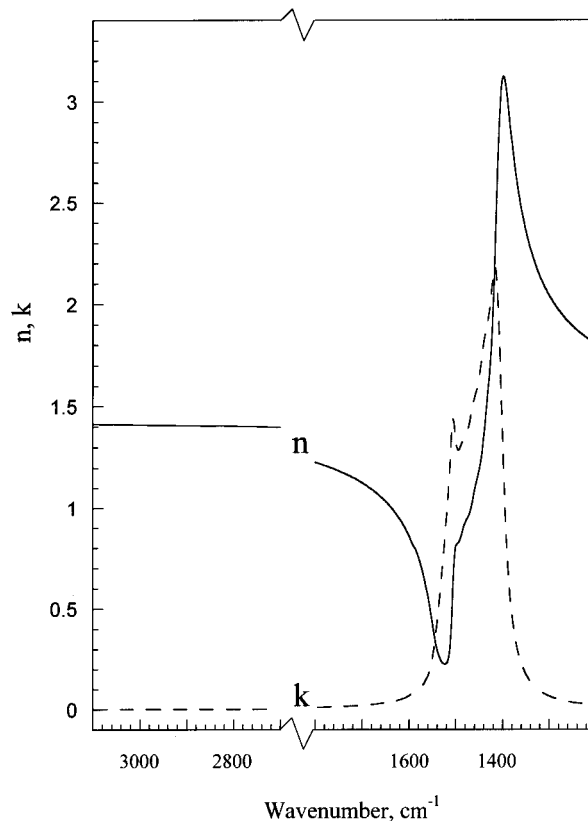


Figure 4. Optical constants: refractive index, n , and absorption coefficient, k , as functions of wavenumber for p-polarization for the cleavage calcite sample.

adsorption (R). Small changes in the sample position between reference and sample spectra will produce differences which

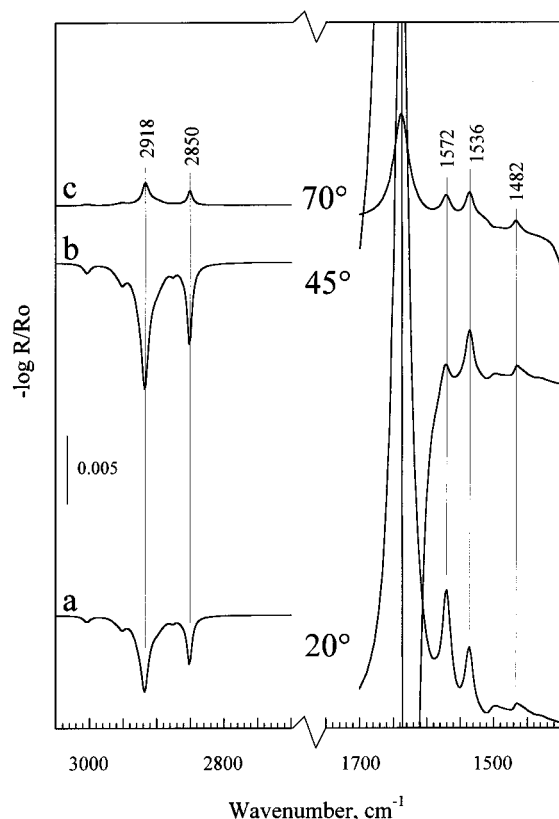


Figure 5. Simulated reflection spectra of an isotropic 2.1 nm hypothetical monolayer of calcium oleate on calcite for p-polarization at incident angles of (a) 20°, (b) 45°, and (c) 70°, for two most characteristic aliphatic and carboxylate wavenumber regions.

are not related to the adsorption layer formation. This phenomenon is illustrated in Figure 3 where reflection spectra of the adsorbed layer of oleate on calcite are recorded in the same position as the reference spectrum of calcite before adsorption (Figure 3a), turned 180° (Figure 3b), and turned about 8° around the axis vertical to the surface plane (Figure 3c). This also clearly indicates that the optical properties of the calcite sample for the spectral simulation of the adsorbed layer have to be determined in exactly the same conditions as the spectroscopic characterization of the adsorption layer. As a consequence, calcite samples cleaved in an identical way were used to determine the optical properties and the nature and structure of the adsorbed layer.

Optical properties of calcite were determined by applying the recently described reflection method.¹⁹ In this method, the optical properties are determined from numerous infrared reflection spectra recorded at different angles of incidence and two polarizations. For calcite, which is an anisotropic mineral, the situation is more complex. For s-polarization, where only one electric field vector parallel to the interface is present, the optical properties of the calcite sample can be calculated from several reflection spectra recorded at different incident angles. Limitation of the spectral investigation to s-polarization means a restriction of the studies to the vibration parallel to the interface. For p-polarization, each spectrum recorded at a different angle will have a different ratio between the vertical and parallel to the interface absorbance components. Hence, for each incident angle, somewhat different optical properties are expected in the x and z directions of the plane of the incident beam. In this study, the best fit of the three reflection spectra of calcite recorded at 20°, 45°, and 70° gives the values of optical constants n and k for p-polarization (Figure 4) which

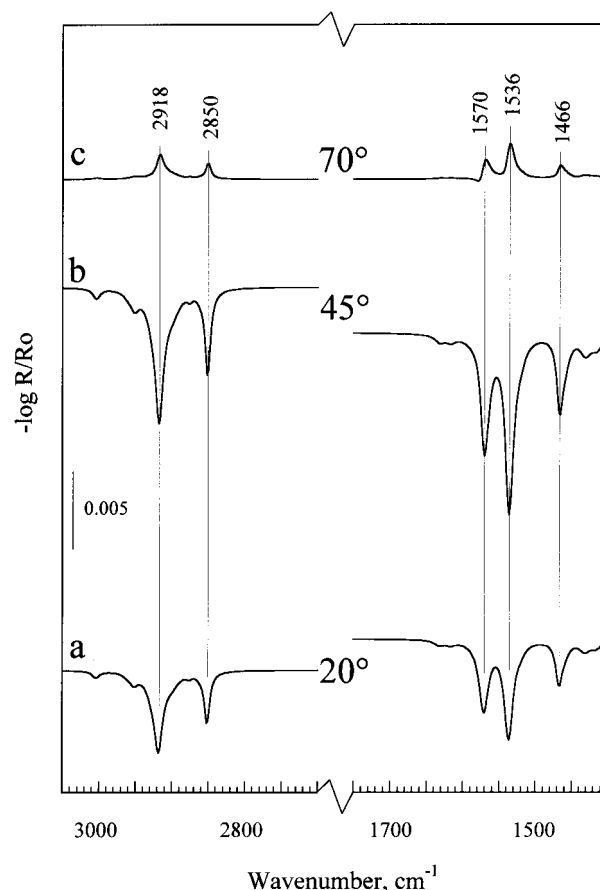


Figure 6. Simulated reflection spectra of an isotropic 2.1 nm hypothetical monolayer of calcium oleate on fluorite for p-polarization at incident angles of (a) 20°, (b) 45°, and (c) 70°.

were used in the simulation procedure. This procedure allows one to simplify the simulation process. The optical properties of calcite reported by White¹⁷ are calculated for differently oriented calcite samples (cut in c axis, not cleavage plane) and for visible light; they are obviously different from those reported here.

The optical constants of the calcium oleate adsorption layer were taken from a recent paper.⁸ It was assumed that the optical constants of the adsorption layers are very similar to those of the precipitated calcium oleate complex. This is obviously a crude assumption at least at the less than monolayer coverages. Nevertheless, it is shown that the experimental spectra recorded with different incidence angles for p-polarization can be well reproduced by spectral simulation using optical constants of precipitated calcium oleate. A discussion of this problem will be presented in the following sections.

Spectral Simulation of the Adsorbed Layer. The spectral simulations were made with the use of the exact equations based on Hansen's formulas¹⁴ for a multilayer system of isotropic and homogeneous phases with parallel interface boundaries. The calculations were performed using a three-phase model: phase 1, air with a refractive index of $n_1 = 1.0$ and an absorption coefficient of $k_1 = 0$; phase 2, the adsorption layer; phase 3, calcite sample with optical constants as shown in Figure 4.

On the basis of the theoretical simulation and consideration, similar to those presented recently for oleate–apatite⁸ and oleate–fluorite systems,²⁰ and after taking into account the practical limitations in optical geometry and angular dispersion of the incident beam in commercial spectrometers, the following experimental conditions were chosen for spectroscopic inves-

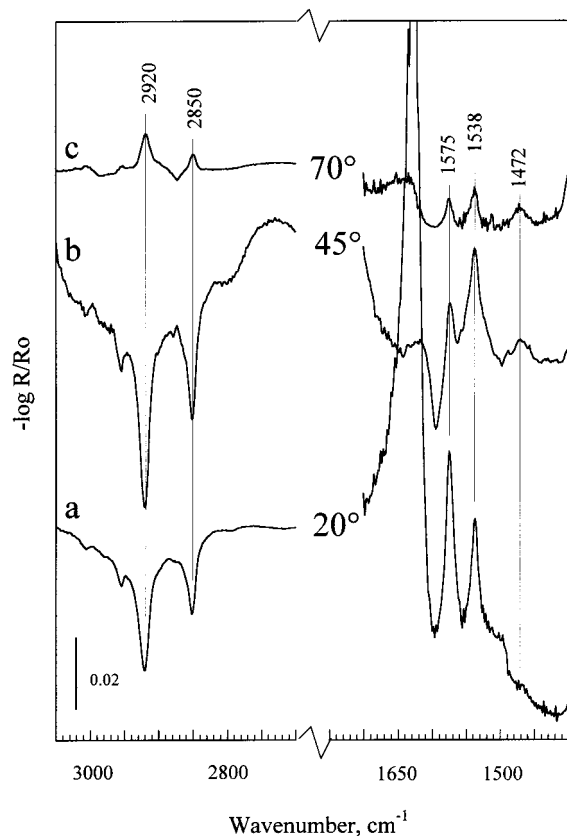


Figure 7. Reflection spectra of calcite after adsorption for 5 min in oleate solution at a concentration of 3.3×10^{-5} M, pH 10, recorded for p-polarization at incident angles of (a) 20°, (b) 45°, and (c) 70°.

tigation of the adsorbed layers of oleate on calcite: for s-polarization, a 20° angle of incidence, for p-polarization, angles of 20°, 45°, and 70°. These experimental conditions ensure spectra of the adsorbed monolayers rich in all structural details and with a high signal-to-noise ratio are obtained.

Simulated reflection spectra of a hypothetical monolayer of calcium oleate on calcite for the chosen optical conditions are presented in Figure 5 for the most characteristic aliphatic and carboxylate vibration regions. The absorbance expected for monolayer coverage (Figure 5) indicates that less than 0.5 of a monolayer of oleate on calcite could be experimentally detected. Since these spectra are calculated for an isotropic layer of calcium oleate, all the observed variations are due to optical effects. Therefore, any difference found between the simulated spectra and the experimental spectra should indicate structural and/or composition changes with regard to the assumed structure of the adsorbed layer.

Comparison of the simulated spectra of a hypothetical monolayer of calcium oleate on calcite (Figure 5) and fluorite (Figure 6) (or with those presented recently for fluorite²⁰ at somewhat different incident angles) shows an interesting influence of the optical properties of the substrate on the recorded band profile. Fluorite, with a refractive index of about 1.4, similar to that of calcite, is almost completely transparent in the infrared region, where calcium oleate shows an absorption. Therefore, it could be an excellent reference in this discussion. The very strong absorption of calcite results in a refractive index below 1 in the region 1480–1600 cm^{-1} . In consequence, very striking differences between calcite and fluorite substrates are observed. First of all, on calcite the only positive bands of the carboxylate group at 1572 and 1536 cm^{-1} are found at incident angles below and above the Brewster angle, $Q_B = 55^\circ$, for an

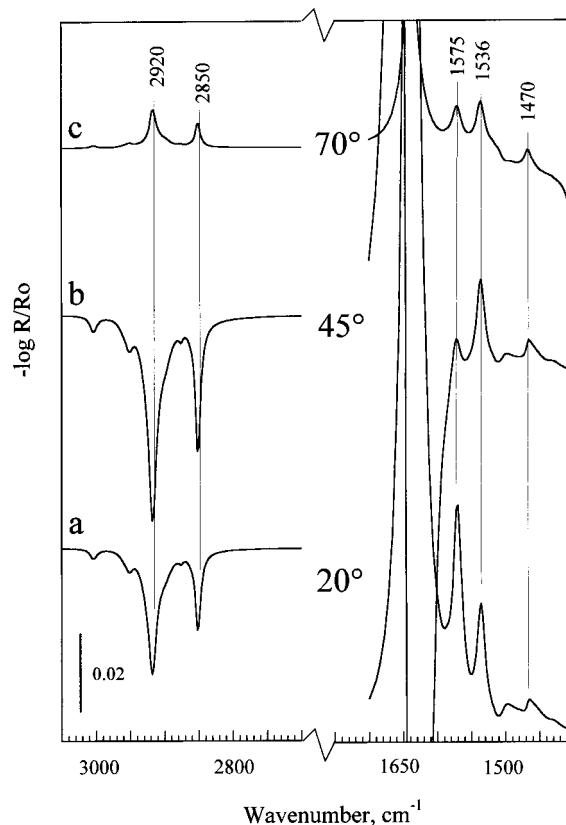


Figure 8. Simulated reflection spectra of an isotropic 14 nm hypothetical layer of calcium oleate on calcite for p-polarization at incident angles of (a) 20°, (b) 45°, and (c) 70°.

isotropic adsorbed layer (Figure 5). This is very different compared to fluorite (Figure 6) or other substrates^{2–8,12} where for incident angles below Q_B the negative absorbance bands are predicted by simulation as well as observed experimentally. The second difference is a very strong absorption band found for calcite at about 1640 cm^{-1} , which is related to strong changes in optical properties of substrate (the change of refractive index from a value below 1 to above 1). This “substrate” band is very sensitive (it can vary from negative to positive) to any small changes in the optical conditions, such as the changes in the angle of incidence and the thickness of the adsorption layer (see also Figure 3). On the contrary, for aliphatic stretching vibrations in the region around 2900 cm^{-1} , where calcite shows optical properties very similar to fluorite, the same simulated spectra were observed (Figures 5 and 6) for both substrates. There are typical changes from negative “absorbance” bands to positive ones when the incident angle of the infrared beam crosses the Q_B .

This discussion indicates that, though there are different optical effects in the case of nonabsorbing and strong absorbing spectral regions, the adsorbed oleate monolayers can be easily monitored by this technique on calcite also in the region of very strong absorption. The influence of a strong variation in the optical properties of the substrate on the recorded spectrum could be predicted and understood as in the case of nonabsorbing substrates.

Adsorption of Oleate on Calcite. Samples of calcite after cleavage without any additional preparation were immersed in oleate solutions with an initial concentration of 3.3×10^{-5} M, at pH 10, for different periods of time. After 5 min of adsorption, the spectra recorded at different incident angles for p-polarization are presented in Figure 7. Comparison of these spectra with

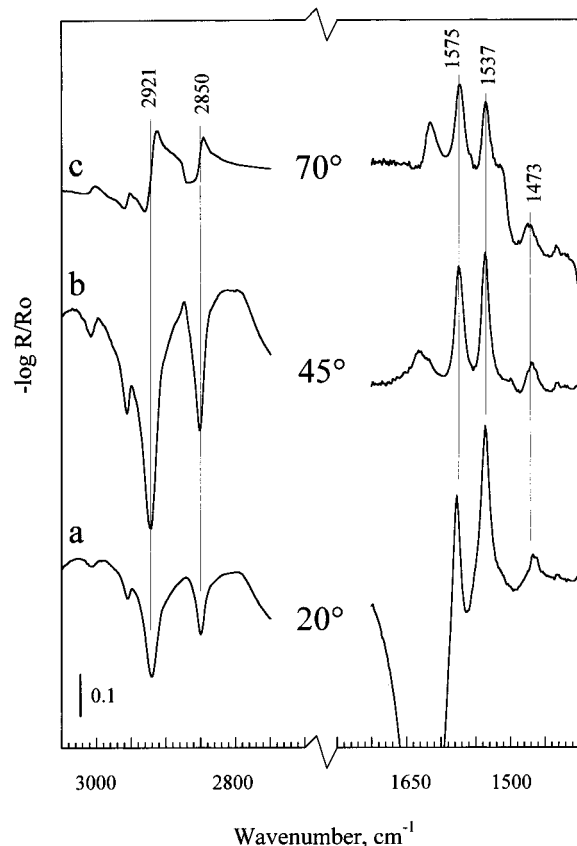


Figure 9. Reflection spectra of calcite after adsorption for 2 h in oleate solution at a concentration of 3.3×10^{-5} M, pH 10, recorded for p-polarization at incident angles of (a) 20° , (b) 45° , and (c) 70° .

the simulated reflection spectra (Figure 8) of a 14 nm thick adsorption layer shows a good agreement between them. The major features of the recording spectra, concerning the absorbance bands at 2920, 2850, 1575, 1538, and 1472 cm^{-1} which are assigned to the adsorption layer of oleate, i.e., the position, shape, and intensity of the absorbance bands, could be accurately predicted by theoretical calculation. Nevertheless, there is a difference in the spectral region of strong changes of optical properties of the substrate, i.e., at about 1630 cm^{-1} , which is caused by strong changes in the electric field vector components at the mineral interface if the refractive index is below 1.⁷ As was already mentioned (see Figure 3), the absorbance band related to calcite is very sensitive to even very small changes in the system under investigation; therefore, this is the spectral region where it is most difficult to simulate correctly the experimentally observed changes. The shape of the band at 1630 cm^{-1} , positive for 20° , negative and positive for 45° , and positive for 70° are the same for the experimental and simulated spectra. The major difference is that the intensities of the band recorded experimentally are much lower than those obtained by calculation. This can be explained by the use of an uncollimated incident beam in a commercial spectrometer, whereas in the simulation, a collimated beam is assumed. With a spread angle of the incident beam of $\pm 5^\circ$ (which is assumed to be characteristic for our optical configuration), the experimental spectrum has to show significantly diminished absorbance bands which are very sensitive to the incident angle, and this is exactly what happens. These differences in the spectral region of about 1630 cm^{-1} could be also affected by the use of the "average" value of the optical constants of calcite for a simulation purpose, whereas in fact they undergo certain variations with the incident angle. Nevertheless, it is important

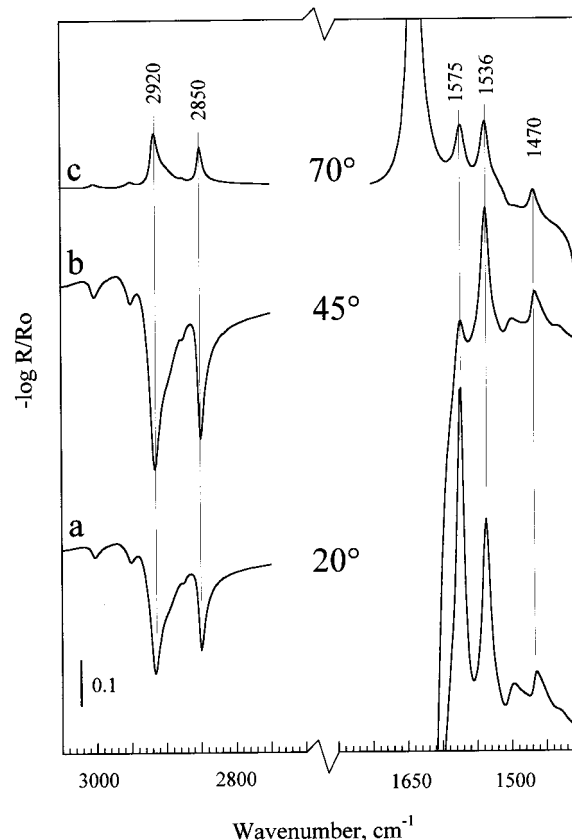


Figure 10. Simulated reflection spectra of an isotropic 150 nm hypothetical layer of calcium oleate on calcite for p-polarization at incident angles of (a) 20° , (b) 45° , and (c) 70° .

to note that this simplification does not produce noticeable modification of the absorbance bands due to the oleate surface species whose spectra can be predicted with good precision because of their much lower sensitivity to the incident angle.

The experimental spectra show very well separated absorbance bands at 1575 and 1538 cm^{-1} at a few oleate monolayers coverage. This indicates the formation of surface calcium carboxylate surface species with two preferential conformations of carboxylate groups: a band at 1575 cm^{-1} , unidentate-like, and a band at 1537 cm^{-1} , bidentate-like conformations, similar to those reported in the case of apatite⁸ and fluorite²⁰ substrates. The good agreement between the experimental and simulated spectra of the oleate adsorbed species indicates that the average thickness of the adsorption layer, whose spectra are presented in Figure 7, is 14 nm, and the structure of the adsorption layer is similar to the structure of precipitated calcium oleate.

Prolongation of the adsorption to 2 h results in the formation of a thicker adsorption layer (Figure 9). At the same time, the strong absorbance band at about 1630 cm^{-1} due to calcite changes from strongly positive (Figure 7a) to strongly negative (Figure 9a). This observation is in agreement with the appropriate simulated spectra (Figures 8a and 10a). However, for the thicker adsorption layer, if the formation of a uniform adsorption layer was assumed, it was not possible to simulate the reflection spectra with the position, shape, and intensity of the absorbance bands, which could fit experimental spectra for three different angles (Figure 9), neither in the spectral region of the absorbance bands assigned to oleate surface species nor for the "substrate" bands. If we consider only the intensity of the absorbance bands, the best fitting of the experimental spectra were obtained for a 150 nm adsorption layer (Figure 10). It was not possible to reproduce better, for example, the characteristic shape and

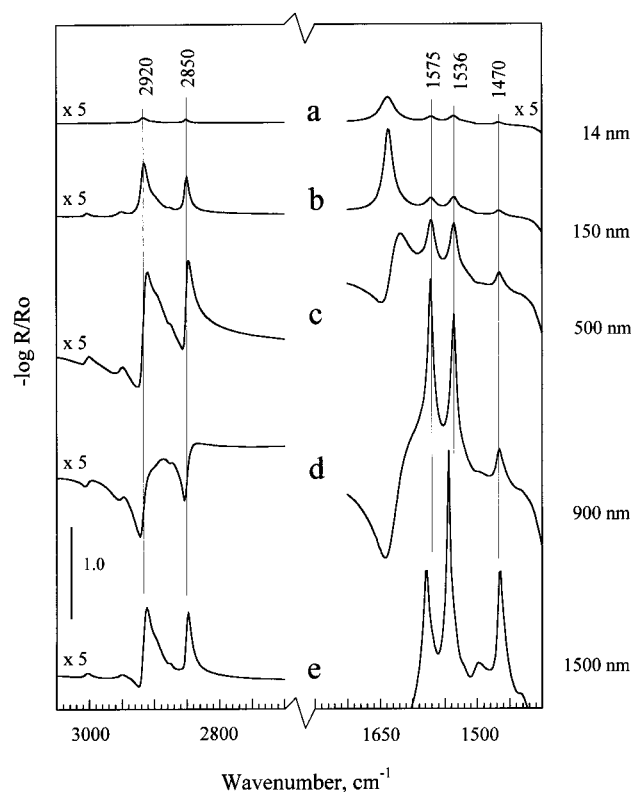


Figure 11. Simulated reflection spectra of an isotropic calcium oleate adsorption layer on calcite for p-polarization at incident angle 70° for different thicknesses (uniform) of the surface layer.

position of the stretching vibration of the aliphatic chain for an angle of incidence of 70° (Figure 9c), keeping the intensity of the absorbance band on the appropriate level. This characteristic shape of aliphatic bands at about 2900 cm^{-1} (Figure 9c) can be simulated for a much higher surface coverage, as could be seen from Figure 11c, where a simulated spectrum for a 500 nm layer at 70° is presented. Thus, these results suggest that the adsorbed species does not form uniform coverage but patches which are about 500 nm high. For the patch surface structure, it is possible to simulate spectra which are similar to those obtained experimentally when about 20% of the surface is covered by 500 nm thick patches. This structure, deduced on the basis of the experimental and simulated spectroscopic data, found full support from microscopic investigation (Figure 12). The optical microscope picture shows clearly visible surface patches with a size of about $1\text{--}2\text{ }\mu\text{m}$, and from atomic force microscope (AFM) measurement it was found that the height of the patches is between 300 and 600 nm. This surface structure is produced by a nucleation and growth mechanism.

If the adsorption layer is distributed unevenly in the form of patches, there are two unknown parameters: the part of surface covered by patches and the height of the patches (or their distribution). Figure 11 shows clearly that there is a very specific relationship between the position, shape, and intensity of absorbance bands in reflection spectra and the thickness of the surface layer. For example, the intensities of the stretching vibration bands of the aliphatic chain at about 2900 cm^{-1} do not increase significantly above coverage higher than 200 nm, whereas the shape of the bands, including transitions from positive to negative absorbance and the inverse, varies significantly. At the same time, the intensities of carboxylate bands increase with coverage, and then at the highest coverage (Figure 11e), they change their position and shape dramatically. These

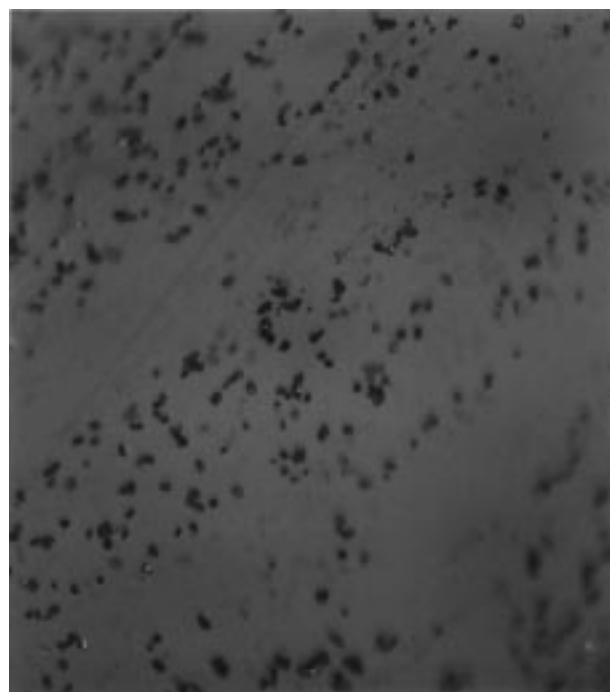


Figure 12. Optical microscope picture of calcite with thick adsorption layer showing patchlike structure with a patch dimension of $1\text{--}2\text{ }\mu\text{m}$. Scale: $1\text{ cm} = 12\text{ }\mu\text{m}$.

observations could be used to estimate properly the average thickness of the patches and in consequence estimate the part of the surface covered by them. This is a very unique property of the external reflection method compared to other infrared techniques, such as transmission and diffuse reflectance.

Conclusions

It was demonstrated, for the first time experimentally and by spectral simulation, that the adsorbed organic monolayers on the substrate showing a very strong absorption in the region of the characteristic vibrations of the surface species can be studied successfully by the infrared external reflection technique. This technique allowed the nature and structure of surface oleate species adsorbed on calcite at different coverages to be examined in detail. The study demonstrated the unique advantage of external reflection infrared spectroscopy over other infrared techniques to obtain detailed information on interface interaction at a molecular level in different systems including the most complex ones such as biological systems.

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