

Spectroscopic Characterization of the Nature and Structure of Adsorbed Organic Monolayers on Quartz in the Region of Very Strong Absorption of Substrate. Reverse Surface Selection Rule

Ela Mielczarski, Yann B. Duval, and Jerzy A. Mielczarski*

Laboratoire “Environnement et Minéralurgie” UMR 7569 CNRS, INPL-ENSG, B.P. 40, 54501 Vandoeuvre-lès-Nancy, France

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It was demonstrated 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 examining in detail the nature and structure of xanthate ($\text{CH}_3\text{CH}_2\text{OCS}_2^-$) adsorbed layer on copper-activated quartz. There is a very strong variation of optical properties of quartz in the region of Si–O stretching vibration including the refractive index of quartz close to 0 between 1250 and 1100 cm^{-1} . These dramatic changes in the optical properties produce different optical effects, and for this reason, the reflection spectra of the adsorbed layer can be divided in three characteristic parts: (i) above 1250 cm^{-1} , (ii) between 1250 and 1100 cm^{-1} , and (iii) below 1060 cm^{-1} . Above 1250 cm^{-1} , a new band at about 1360 cm^{-1} is observed because of the pure optical effect caused by the refractive index of quartz crossing the value of 1.0. This optical effect, “substrate band”, is very sensitive to the thickness of the adsorbed layer and was utilized in this work for the determination of the patch-like structure of the produced adsorbed layer. In the second region between 1250 and 1100 cm^{-1} , where the refractive index of quartz is close to 0, only the electric field vector component parallel to substrate interface ($\langle E_x^2 \rangle$ for p polarization) shows significant value, and as a consequence, only molecular vibration parallel to interface can be monitored for p polarization. This important finding is exactly reverse to the phenomenon observed at metal interfaces in the infrared region where practically only the vertical vibration (strong $\langle E_z^2 \rangle$ component) could be spectrally monitored and is known in the literature as the “surface selection rule”. Hence, a “reverse surface selection rule” could be postulated for the adsorbed species investigated in the region of strong absorbance of substrate at refractive index significantly lower than 1.0. The highest spectral sensitivity to monitor the adsorbed species was found at the lowest incident angles (close to zero), which is another reverse observation compared to metal substrates where a grazing incident angle is recommended as the most sensitive spectral condition. In the third region below 1060 cm^{-1} , complex optical effects are observed resulting from a sharp decrease of the refractive index of quartz from a value around 5 to 2. It can be subdivided in two parts: (i) a higher refractive index (more than 3) that results in positive absorbance bands below Brewster angle and (ii) a lower refractive index that results in negative absorbance bands below Brewster angle. Another important phenomenon that has a strong effect on the recorded reflection spectra at higher incident angles is a strong shift of the Brewster angle with wavenumber. All of these complex optical effects were identified and described. This allowed interpreting properly the spectroscopic data and in consequence to describe in detail the surface phenomena that take place during the formation of the xanthate adsorption layer on copper-activated quartz. This work shows that the complex optical phenomena taking place during reflection of an incident beam in a stratified system are an enormous source of detailed information on the nature and structure of the produced surface layer even in such difficult systems with overlapping of very low signal from adsorbed species with very strong absorbance of substrate.

Introduction

With the development of FT-IR spectrophotometers over the past two decades, the utility of infrared spectroscopy for characterization of adsorbed layers on metallic and nonmetallic substrates at a molecular level has increased enormously. However, if the substrate shows very strong absorbance bands that overlap the very low intensity bands of the adsorbed monolayers, the monitoring of surface phenomena is very difficult or even impossible with the use of transmission or diffuse reflectance techniques. For such measurements, the

signal would be very weak with respect to background variations, and the recording of good quality spectra of adsorbed species would be very difficult or impossible. An application of the recently developed curve fitting procedure (for example ref 1) of overlapped signals from different components was a failure. In a recent work,² it was demonstrated that the utilization of infrared external reflection technique makes it possible to monitor carboxylate groups of the adsorbed oleate monolayers on calcite, even in the region of very strong absorption by carbonate groups of substrate.

This work demonstrates the possibility to determine in detail the nature of the adsorbed species and their surface distribution on quartz from recorded reflection spectra in the region of very

* To whom correspondence should be addressed. E-mail: jerzy.mielczarski@ensg.inpl-nancy.fr.

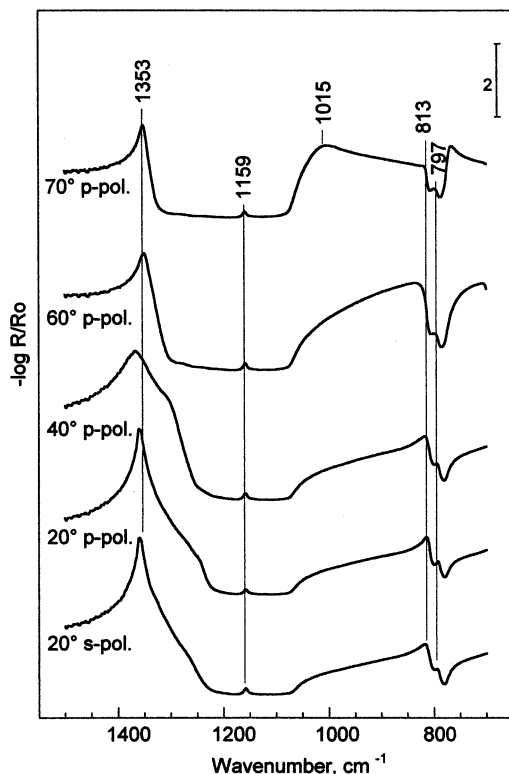


Figure 1. Reflection spectra of quartz before adsorption recorded for s and p polarizations at incident angles 20°, 40°, 60°, and 70°. The reference spectrum was aluminum mirror; the DTGS detector was used in the measurement.

strong absorbance of the substrate. For this reason, detailed consideration of optical phenomena in spectral regions of very strong absorbance of quartz (between 950 and 1250 cm^{-1}) and its close vicinity were carried out. These studies were performed for quartz with an adsorbed layer that produces hydrophobic properties. The surface modification was carried out in a two-step process. At first, the quartz surface was activated by copper ions, and then adsorption of ethyl xanthate ions ($\text{CH}_3\text{CH}_2\text{OCS}_2^-$) was performed. This short chain molecule shows the strongest and most characteristic infrared absorbance of the head molecular groups (COC and SCS), between 1000 and 1200 cm^{-1} .³ In the same region, quartz has a very strong absorbance⁴ because of the Si–O stretching vibrations.

Experimental Section

Materials. Natural mineral samples of quartz (Madagascar) with dimensions of about $10 \times 20 \text{ mm}^2$ with one side polished were used in this study. Quartz was a very high purity transparent crystal. X-ray diffraction confirmed the α -quartz polycrystalline structure. The polycrystalline structure of the quartz sample can be also deduced from infrared reflection spectra presented in Figure 1 (two bands at around 800 cm^{-1}). The potassium ethyl xanthate used in these studies was synthesized from CS_2 , KOH, and ethyl alcohol and then purified by recrystallization from acetone and ether. Other reagents were all of an analytical grade. Distilled water from the Millipore (Milli-Qplus, 18 M Ω cm) system was used throughout the experiments.

Adsorption Studies. The quartz sample was polished with emery paper and alumina powder. The final polishing was made with the use of 0.05 μm alumina, and the polished sample was washed with water. Quartz was immersed in 200 mL of copper solution at a concentration of $5 \times 10^{-4} \text{ M}$ for 30 min and then

transferred to a xanthate solution for 30 min of adsorption. The pH of all used solutions, including washing water, was 8.0 ± 0.1 . The xanthate solution concentration was $5 \times 10^{-4} \text{ M}$. Immediately after adsorption in xanthate solution, the sample was immersed in water with a pH of 8 for about 1 s, to remove possible drops of xanthate solution and then placed instantly in an FT-IR spectrophotometer to record the reflection spectra.

Infrared Analysis. The infrared reflection spectra of slab samples were recorded on a Bruker IFS55 FT-IR spectrometer equipped with an MCT or DTGS detector and a reflection attachment (Seagull). A wire-grid polarizer was placed before the sample and provided p- or s-polarized light. These accessories were from Harrick Scientific Co. For each adsorption layer, usually five reflection spectra were recorded by the use of s- and p-polarized light and different angles of incidence, 20°, 50°, 60°, and 70°. Other details of experimental procedure can be found in our recent paper.⁵ An optimized optical reflection system permits us to detect the adsorbed amount as low as about 30% of a statistical monolayer of copper xanthate on quartz surface, which is equivalent to a 0.2 nm thick uniform layer of copper xanthate. 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 adsorbed layer, respectively. Both sample and reference spectra are averaged over the same number of scans, from 200 to 3000 scans, depending on energy throughput.

Results and Discussion

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 requires a carefully designed experimental procedure. It was discussed in detail in recent papers.^{2,3,5–18} 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 experimental reflection spectra as well as for optimization of the experimental conditions.

Adsorption of Xanthate on Copper-Activated Quartz.

Reflection spectra of the same quartz sample recorded after activation and adsorption are shown in Figure 2 for different incident beam angles and two polarizations. These spectra show numerous positive and negative bands, and some of them vary significantly in intensities depends on angle of incidence. Understanding the origin of the observed changes in the recorded spectra is fundamental to describe the nature and structure of the produced adsorbed layer. There is no spectroscopically detectable xanthate adsorption on quartz without earlier copper activation. The hydrophobic layer produced by xanthate adsorption is due to the formation of a surface copper xanthate complex. There are absorbance bands at about 1197, 1124, 1050, 1033, and 1010 cm^{-1} that can be assigned to the copper xanthate

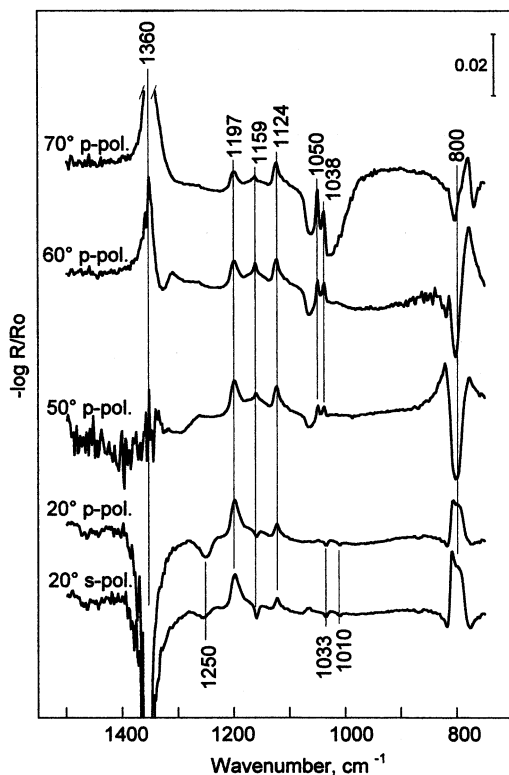


Figure 2. Reflection spectra of the adsorbed layer of ethyl xanthate on copper-activated quartz after adsorption at pH 8 recorded for s and p polarizations at incident angles 20°, 50°, 60°, and 70°.

complex.³ However, the relative intensity of these bands and their positive and negative signs in the same spectrum are very unusual features. There is also a very strong band at about 1360 cm^{-1} with positive and negative intensities and other bands at about 1250, 1159, and 800 cm^{-1} that vary with angles of incidence of the infrared beam. All of these features need to be explained before any conclusion about the nature of the surface complex formation and its surface structure are reached. At first, we have to distinguish the spectral features resulting from the presence of adsorbed species from those that originated from optical effects because of a strong absorbance of quartz and then to interpret them correctly. These are the main aims of the presented work.

Optical Considerations. *Quartz.* Quartz shows a very strong absorbance between 1250 and 1000 cm^{-1} and at about 800 cm^{-1} (Figure 3a) assigned to asymmetric and symmetric stretching vibrations of the Si—O—Si groups.¹⁹ The reflection spectra of quartz before adsorption recorded at different angles of incidence (Figure 1) show in the region of strong absorbance a plateau. The range of the plateau is wider at 70° (between 1320 and 1090 cm^{-1}) than at 20° (between 1250 and 1080 cm^{-1}). Between 1250 and 1100 cm^{-1} , quartz shows a reflection index very close to zero, below 0.2 (Figure 3a). There is a very small band at 1159 cm^{-1} (Figure 1), which is due to the changes in optical properties of quartz (Figure 3a). Analysis of the variation of optical properties of quartz with frequency indicates that the band at 1360 cm^{-1} is caused by the changes of refractive index of quartz that passes from a value above 1.0 to below 1.0 with the absorbance coefficient very low. A similar observation was reported recently for the calcium carbonate substrate.² It is interesting to note that the reverse crossing of the refractive index (extraordinary dispersion) from a value below 1.0 to above 1.0, in the region where a very strong absorption coefficient is observed, results in much smaller spectral variation (absorbance gap at about 1070 cm^{-1}) than that observed at 1360 cm^{-1} .

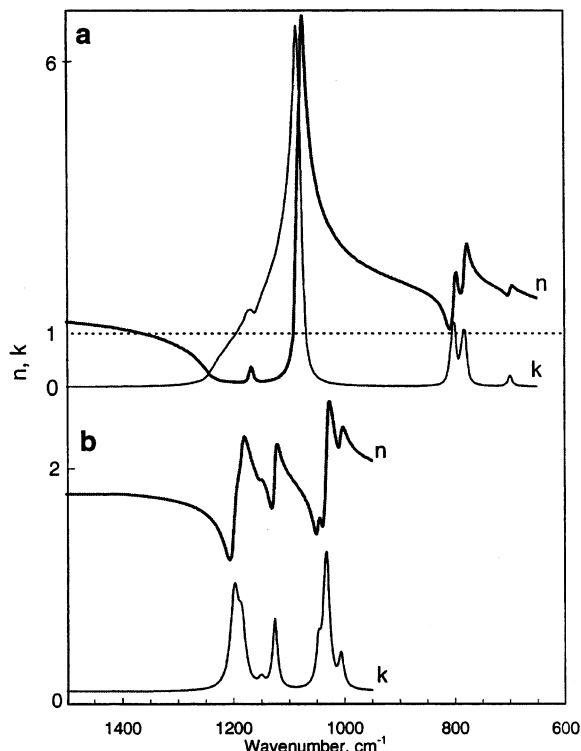


Figure 3. Optical constants: refractive index n , and absorption coefficient k , as functions of wavenumber for (a) polycrystalline quartz (after ref 4) and (b) cuprous ethyl xanthate (after ref 21).

The other observed bands around 800 cm^{-1} show a classical behavior. These bands are assigned to the Si—O symmetric stretching vibrations perpendicular and parallel to the optic axis of quartz. For two polarizations at 20° (Figure 1), these bands show almost the same intensity and shape, indicating the polycrystalline structure of the used quartz sample.

Quartz with a Hypothetical Monolayer of the Copper Ethyl Xanthate Complex. The spectral simulations were made with the use of the exact equations based on Hansen's formulas²⁰ 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; and phase 3, quartz sample, with optical constants as shown in Figure 3a. These optical constants are calculated for the polycrystalline sample from the reported data for crystalline quartz.⁴ Optical constants for the adsorption layer of the copper ethyl xanthate complex (Figure 3b) were taken from recent work.²¹

On the basis of theoretical simulation of the reflection spectra of hypothetical adsorbed layer for various incident angles and polarizations, 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 investigation of the adsorbed layers of xanthate on quartz: for s polarization, a 20° angle of incidence; for p polarization, angles of 20°, 50°, 60°, and 70°. These experimental conditions ensure the possibility to obtain spectra of the adsorbed monolayers rich in all spectral details and with a high signal-to-noise ratio.

Simulated reflection spectra of a hypothetical monolayer, i.e., 0.8 nm thick layer of copper xanthate on quartz for the chosen optical conditions, are presented in Figure 4 for the most characteristic xanthate headgroup vibration (ν COC and ν SCS) bands between 1200 and 1000 cm^{-1} . The spectra calculated for

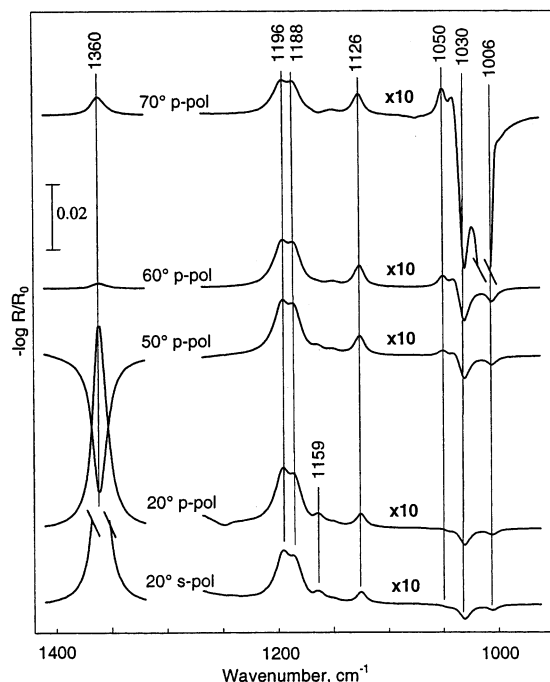


Figure 4. Simulated reflection spectra of an isotropic 0.8 nm hypothetical monolayer of cuprous ethyl xanthate on quartz for p polarization at incident angles 20°, 50°, 60°, and 70° and for s polarization at 20°, in the most characteristic wavenumber regions. (Note different absorbance scale for the two spectral regions.)

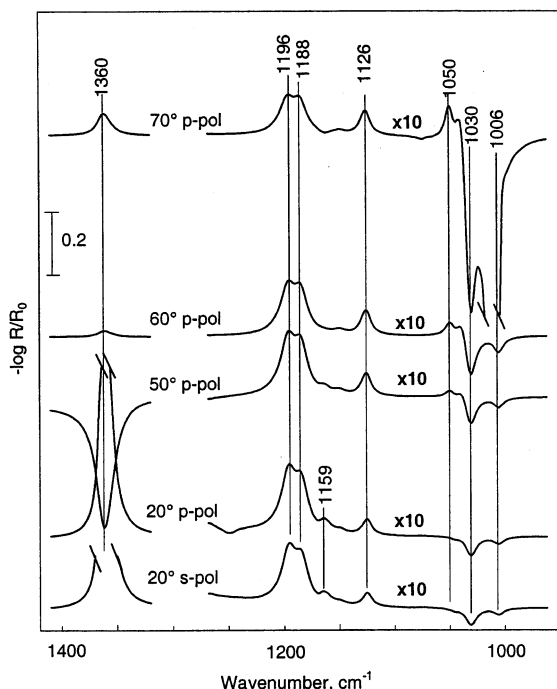


Figure 5. Simulated reflection spectra of an isotropic 10.5 nm hypothetical monolayer of cuprous ethyl xanthate on quartz. Other conditions as in Figure 4.

10.5 and 35 nm thick layers are presented in Figures 5 and 6. A close comparison of these results reveals that in this range of thickness the intensities of the absorbance bands of the adsorbed xanthate layer are proportional to the amount adsorbed. Moreover, the shapes of the characteristic absorbance bands are almost exactly the same. On the contrary, the changes in the shape and intensity of the band about 1360 cm^{-1} are dramatic if the amount adsorbed increases above 11 nm.

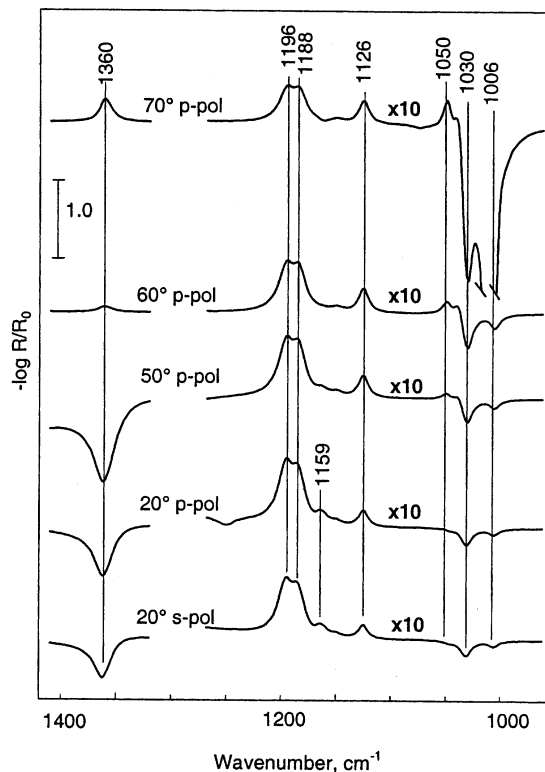


Figure 6. Simulated reflection spectra of an isotropic 35 nm hypothetical monolayer of cuprous ethyl xanthate on quartz. Other conditions as in Figure 4.

Because of the strong changes in optical properties of quartz (Figure 3a) and related to them different optical effects will be discussed in three spectral regions: (i) above 1250 cm^{-1} , (ii) between 1250 and 1100 cm^{-1} , and (iii) below 1060 cm^{-1} . We will demonstrate that the observed spectral features in these three regions result from different optical effects.

Below 1060 cm^{-1} , three characteristic absorbance bands of the adsorbed product are present at about 1050, 1030, and 1006 cm^{-1} . The bands at 1050 and 1030 cm^{-1} are due to almost pure stretching vibrations of the COC and SCS groups, respectively (ref 3 and see also Figure 12). These bands have been already used to determine orientation of xanthate molecules in adsorption layers on various substrates.^{14,22} In this spectral region, the most complex optical effects are observed resulting from a sharp decrease of refractive index of quartz from a value around 5 to 2 which results in very strong variations of optical conditions for a particular wavenumber. To understand these phenomena, the changes of the absorbance components, A_X , A_Z , and $A_{\text{TOTAL}} \sim A_X + A_Z$, at the interface have to be analyzed. These absorbance components have very close relationships with the experimentally recorded absorbance for p polarization (for details see refs 3 and 11). The simulated absorbance components calculated for the three characteristic xanthate absorbance bands at 1050, 1030, and 1006 cm^{-1} are presented in Figure 7. At 1050 cm^{-1} , where the refractive index of quartz is of 4.05 the simulated absorbance, A_{TOTAL} , is small and negative at lower angles of incidence below 28°. When the incident angle increases, the absorbance changes sign from negative to positive at about 28° and becomes strongly positive just before the Brewster angle (θ_B) ($\theta_B = 76^\circ$ for this frequency). This behavior is characteristic for the substrate with a high refractive index and was already reported for copper sulfide substrates.^{3,11,23} A reverse situation is observed at 1030 cm^{-1} where the refractive index of quartz drops to 3.1. The simulated absorbance, A_{TOTAL} ,

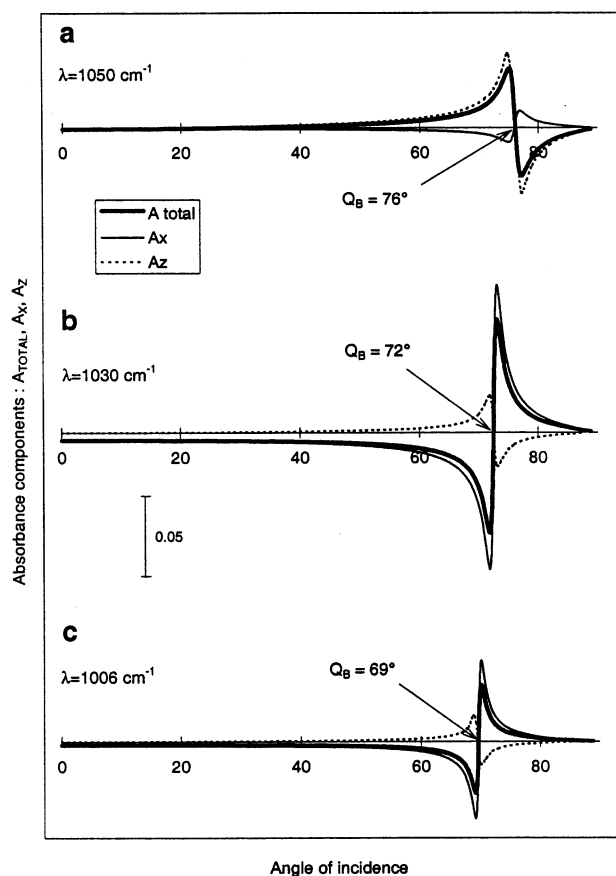


Figure 7. Simulated absorbance, A_{TOTAL} , and absorbance components, A_X and A_Z , of isotropic 0.8 nm layer of cuprous ethyl xanthate on quartz at 1050, 1030, and 1006 cm^{-1} as a function of incident angles for p polarization.

(Figure 7b) is negative for all angles below the Brewster angle ($\theta_B = 72^\circ$ for this frequency). The highest negative intensity is expected at an incident angle close to 70° . This relationship is characteristic for the substrates with low refractive index as was already reported for substrates such as fluorapatite, $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$,⁵ fluorite, CaF_2 ,²⁴ and tetrahedrite, $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$.²³ The different optical effects for 1050 and 1030 cm^{-1} bands result from the differences in relative intensity of the A_Z and A_X components at the angles of incidence just below the Brewster angle. For a substrate with a high refractive index, as in the case of the band at 1050 cm^{-1} for quartz (Figure 7a), the A_X component is much lower than the A_Z component, resulting in the observation of a positive band in the simulated spectrum at 70° . A reverse situation is found for a substrate with a low refractive index, which is the case for the band at 1030 cm^{-1} for quartz (Figure 7b), the A_X component is much higher than the A_Z component and as consequence a negative band is predicted for this frequency. As consequence of the transition between these two optical effects, a positive band at about 1040 cm^{-1} is produced in simulated spectra at 70° (Figures 4–6). At 1006 cm^{-1} , the refractive index of quartz is 2.4; hence, the simulated changes in absorbance with angle of incidence are similar to those found for the band at 1030 cm^{-1} (Figure 7 parts b and c). At this spectral region, there is another optical effect that is related to phenomena of passing the Brewster angle. At 1006 cm^{-1} $\theta_B = 69.6^\circ$, hence, the recorded spectrum at 70° will be in very close vicinity to the Brewster angle where simulated absorbance components change dramatically (Figure 7c). The very strong complex negative band at about 1010 cm^{-1}

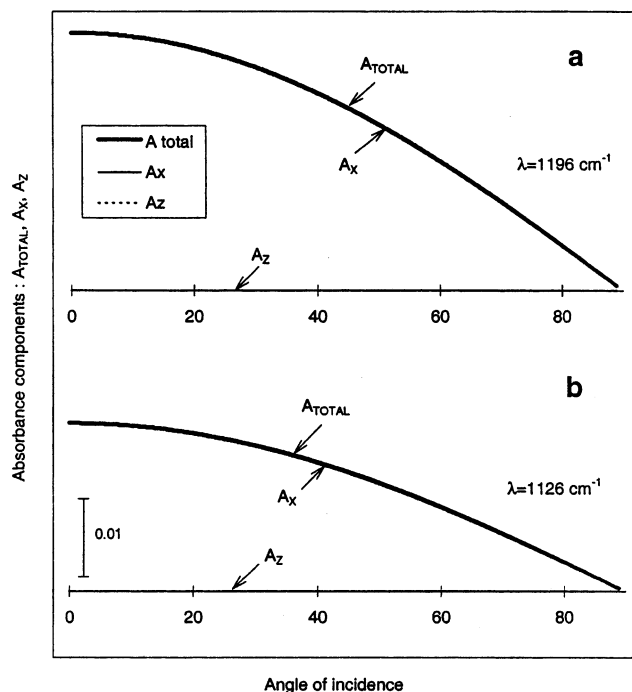


Figure 8. Simulated absorbance, A_{TOTAL} , and absorbance components, A_X and A_Z , of isotropic 0.8 nm layer of cuprous ethyl xanthate on quartz at 1196 and 1126 cm^{-1} as a function of incident angles for p polarization.

found in simulated spectrum at 70° (Figures 4–6) is a consequence of the phenomenon.

In the second region, between 1250 and 1100 cm^{-1} , the refractive index of quartz is in the vicinity of zero (Figure 3a). The calculated absorbance components for the bands at 1196 and 1126 cm^{-1} show that the A_X component is almost exactly the same as the A_{TOTAL} component over the entire range of incident angles from 0 to 90° (Figure 8). The A_Z component is very low and, thus, practically does not have any influence on the recorded spectrum. As a consequence of these very specific optical conditions, it is possible to monitor for p polarization only molecular vibrations parallel (or with components parallel) to the substrate plane. This important finding is perfectly reverse to the phenomenon observed at metal interfaces in the infrared region where practically only the vertical vibration, the A_Z component, of the species in a thin adsorbed layer could be spectrally monitored.²⁵ This is known in the literature as the “surface selection rule”.²⁶ A “reverse surface selection rule” could be postulated if the adsorbed species are investigated in the region of strong absorbance of the substrate where a close to 0 refractive index is observed. As the simulation shows, clearly, the highest spectral sensitivity to monitor the adsorbed species was found at the lowest incidence angles (close to 0), which is another reverse observation compared to the metal substrates where a grazing incident angle is recommended as the most efficient experimental condition.

In the third region, above 1250 cm^{-1} , absorbance of quartz is very low, and the refractive index is below or somewhat above the value of 1.0 (Figure 3a). There is a band at 1360 cm^{-1} due to the optical effect caused by the crossing of the value of 1.0 by the refractive index of quartz. This band, namely the “substrate band”, is due to the specific variation of the substrate optical properties. It is very sensitive to the presence of the adsorbed layer. The intensity of the band as well as its positive or negative absorbance vary tremendously with changes of thickness of the adsorbed layer, which plays a role of an

intermediate phase producing interference component (Figures 5 and 6). This unique optical effect could be employed for quantitative evaluation of the structure of the adsorbed layer. For example, it can be used for the determination if the adsorbed species are uniformly distributed on substrate or form patches with specific size and height. This phenomenon is applied in the next section for the determination of the structure of the produced hydrophobic xanthate layer on quartz.

Discussion of the Experimental Results. The simulated reflection spectra are calculated for an isotropic layer of copper xanthate. Therefore, the differences found between the simulated spectra and the experimental spectra could indicate structural or/and composition changes with regard to the assumed composition and structure of the adsorbed layer. Optical effects discussed in previous sections are another source of the observed differences. Keeping these in mind, the analysis of the experimental spectra of the adsorbed layer was performed.

Comparison of the simulated spectra of a hypothetical monolayer of cuprous xanthate on quartz (Figure 4) and the experimental spectra of the adsorbed layer (Figure 2) shows several striking features. At first, it can be concluded based on the observed band positions that the adsorbed product is, in fact, the cuprous xanthate surface complex. The intensity of the absorbance bands are much higher than expected for monolayer (0.8 nm) coverage. Moreover, the relative intensity ratios of the recorded band are not as predicted from the simulated data for an isotropic layer. This could indicate an orientation of the adsorbed molecules in the surface layer.

The determination of the orientation of the molecular cuprous xanthate species at the interface of a different substrate were already reported.^{14,22,27} The calculation was done based on the relative intensity of the absorbance bands at 1050 and 1030 cm^{-1} , which were found as the almost pure vibrations of the asymmetric stretching of the COC and SCS molecular groups.³ Unfortunately, this procedure cannot be applied successfully here because in this spectral region the absorbance bands at low angles of incidence show almost the same value (Figures 4 and 5) and at angles close to the θ_B are strongly perturbed by the dramatic variation in absorbance and the shift of the Brewster angle value with wavenumber and the angle of incidence (Figure 7). The experimental spectra are recorded by a commercial spectrometer where the incident beam is not collimated. There is an about $\pm 5^\circ$ spread angle of the incident beam. These together make very difficult the determination of the orientation angle of the adsorbed xanthate molecular group with good precision. Therefore, another procedure was developed based on the finding that the absorbance band at 1126 cm^{-1} is due to the almost equal mixture of the stretching vibration of the COC and SCS molecular groups (ref 3 and references therein). For this reason, it can be assumed that the band shows the lowest sensitivity to any changes in molecular orientation at interface.

A good fitting of the experimentally recorded absorbance band at about 1120 cm^{-1} at 20° and 60° incident angles can be obtained with the assumption of the 10.5 nm thick surface layer for simulation procedure (Figure 9). However, for this thickness of the adsorbed layer, the other characteristic cuprous xanthate absorbance bands show much lower intensity in the experimental spectra than in the simulated ones for an isotropic layer (Figure 9). This indicates, as was already mentioned earlier, a particular orientation of the COC and SCS molecular groups. The much lower intensity of the bands at about 1030 cm^{-1} suggests that the dipol moment of the asymmetric stretching vibration of the SCS group (Figure 12) has preferential vertical orientation to the substrate interface. The very rough estimation performed

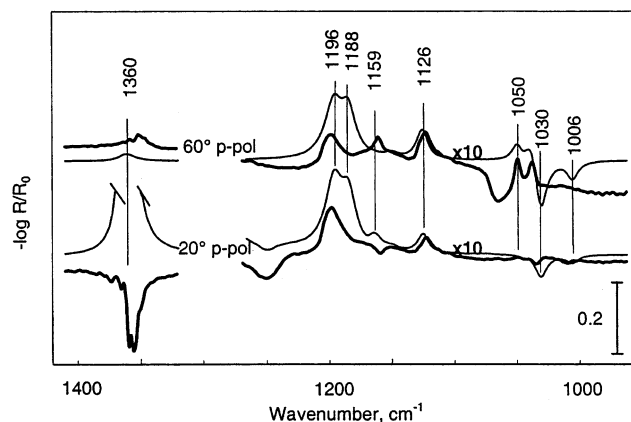


Figure 9. Comparison of experimental reflection spectra (thick line) of xanthate adsorption layer on activated quartz with simulated spectra (thin line) of isotropic 10.5 nm layer of cuprous ethyl xanthate on quartz for p polarization at 20° and 60°.

(see discussion in the paragraph above) indicates the orientation angle Φ_1 about 30° to the surface normal (Figure 12).

The determined nearly vertical position of the dipol moment of the stretching vibration of the SCS group is in agreement with the observed experimentally lower intensity of the bands at about 1197 cm^{-1} compared with the simulated ones. These bands are due to the complex stretching vibrations of the COC and SCS groups. As was explained in the previous section at this frequency, only molecular groups with a dipol moment parallel to substrate interface can be monitored; hence, the absorbance caused by the SCS vibration with nearly vertical orientation cannot be observed in the recorded spectrum. Therefore, the experimentally observed band at 1197 cm^{-1} (Figure 2) is mainly due to the COC stretching vibration with its dipol moment nearly parallel to the interface. This finding agrees with the changes in relative intensity of the band at 1050 cm^{-1} that is almost pure asymmetric stretching vibration of the COC molecular group. The very rough estimation carried out indicates that the orientation angle Φ_2 of the dipol moment of the COC group is about 60° to the surface normal (Figure 12).

The adsorbed xanthate species on copper-activated quartz show nearly flat molecular position versus substrate interface, which is contrary to the vertical position observed for ethyl xanthate adsorption on copper,¹⁰ and cuprous sulfide^{14,27} substrates where orientation angles are between 70 and 85° and 40–50° for the SCS and COC molecular groups. This indicates a very specific structure of the cuprous xanthate on activated quartz compared to other substrates and suggests different mechanisms of the surface layer formation depending on substrate.

For the thickness of the adsorbed layer of 10.5 nm, it is not possible to fit the experimental spectra in the spectral region around 1360 cm^{-1} . Only the strong positive absorbance band about 1360 cm^{-1} is visible in the simulated spectrum at 20°, whereas the experimental spectrum shows this band strongly negative (Figure 9). This very strong negative band can be simulated with good precision if the thickness of the adsorbed layer is assumed bigger than 35 nm (Figure 10). For the assumed thickness of 35 nm the characteristic absorbance bands for the adsorbed xanthate molecules in the experimental spectra are about 3.5 times lower than those obtained from the calculation. This suggests a patch-like structure for the adsorbed layer. A very good fitting of the experimental spectra at different angles was found when simulation was performed with the assumption that 30% of quartz surface is covered by 35 nm patches (Figures

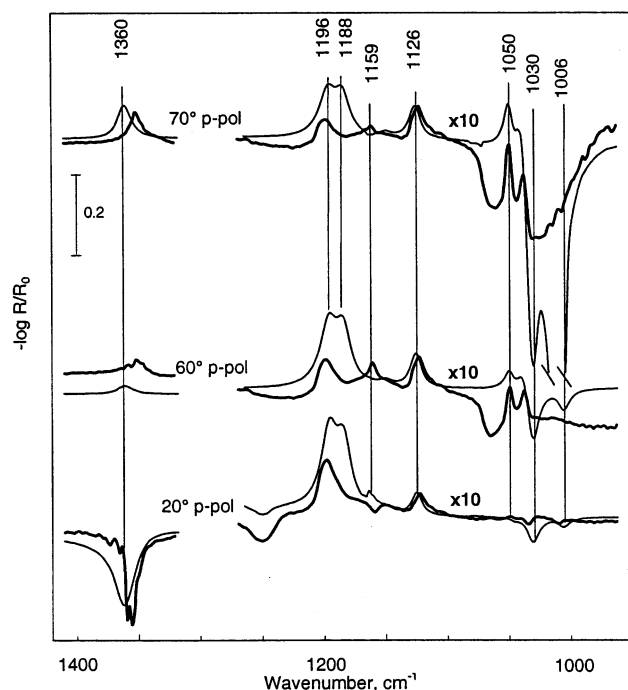


Figure 10. Comparison of experimental reflection spectra (thick line) of xanthate adsorption layer on activated quartz with simulated spectra (thin line) of the adsorbed surface layer contains 35 nm high patches covering 30% of surface.

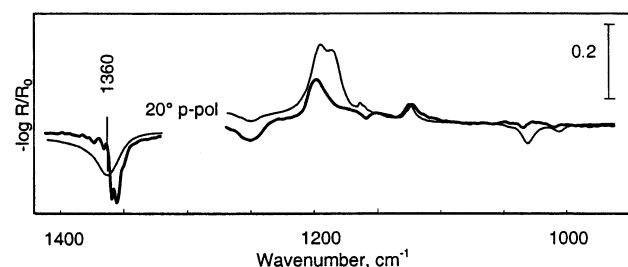


Figure 11. Comparison of experimental reflection spectra (thick line) of xanthate adsorption layer on activated quartz with simulated spectra (thin line) of the adsorbed surface layer consists of 35 nm high patches covering 30% of surface, and 0.8 nm layer covering 70% of surface, for p polarization at 20°.

10 and 12). Another possible surface structure is monolayer coverage together with 35 nm patches. A simple mathematical average was considered for the total calculated spectrum of these two surface domains. This surface products distribution was found less favorable because worse fitting of the experimental results in region of the band at 1360 cm^{-1} (Figure 11).

The found patch-like structure of the adsorbed cuprous xanthate could explain the difference in the surface structure compared to other copper containing substrates where more uniform growth of the adsorption layer was observed. The produced patches, which can be also microcrystals, can epitaxially grow with a specific orientation characteristic for quartz substrate. This also suggests that the activation of quartz by copper ions results in the formation of surface precipitated copper hydroxide aggregates, which in the second step interact with xanthate producing uneven coverage. Surface diffusion of the adsorbed molecules could be also reason for the patchy structure formation.

Conclusions

It was demonstrated experimentally and by spectral simulation that the adsorbed organic monolayers on the substrate showing

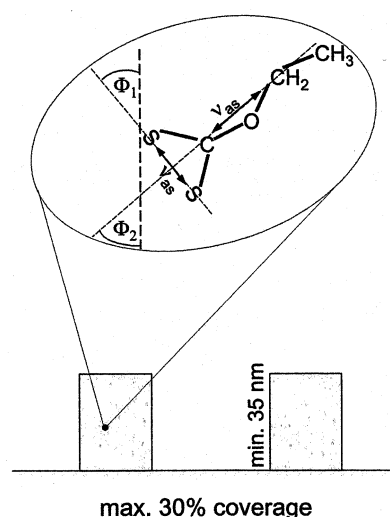


Figure 12. Schematic presentation of the surface distribution of the adsorbed cuprous ethyl xanthate patches with its molecular configuration. The patches are at least 35 nm high, and they cover about 30% of quartz surface.

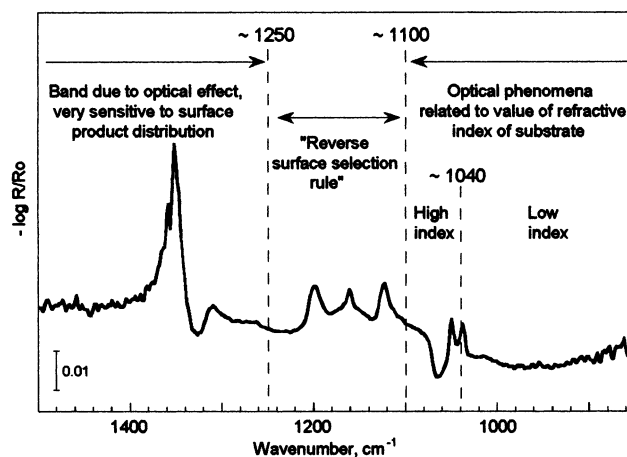


Figure 13. Spectral regions of different optical phenomena taking place at the quartz surface covered by the adsorbed layer.

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. A summary of different optical phenomena taking place at the quartz surface covered by adsorbed layer is presented in Figure 13. A specific optical effect "reverse surface selection rule" is postulated for the adsorbed species investigated in the spectral region of strong absorbance of the substrate when its refractive index is close to 0 (between 1250 and 1100 cm^{-1}). In this case, only parallel to interface vibrations can be monitored with the highest spectral sensitivity at lowest incident angles (close to zero). These are reverse observations compared to the "surface selection rule" established for metal substrates where only vertical to interface vibrations can be monitored at grazing incident angles.

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 for difficult to investigate systems where complete overlapping of the absorbance bands of the adsorbed layer and substrate takes place.

The reflection technique allows examining in detail the nature and structure of surface xanthate species adsorbed on copper-activated quartz. The results suggest that copper ions adsorb on quartz with the formation of surface precipitated copper

hydroxide aggregates. They interact with ethyl xanthate producing surface hydrophobic cuprous xanthate species. The surface product forms patches or microcrystals higher than 35 nm that are unevenly distributed on no more than 30% of the quartz surface.

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