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A SNIFTIRS Study of the Diffuse Double Layer at Single Crystal Platinum Electrodes in Acetonitrile

by

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ABSTRACT

In situ reflection infrared spectroscopy with electrochemical modulation has been used to investigate the structure of the double layer for the system: Pt(hkl) / acetonitrile. The electrolytes used were tetraethylammonium perchlorate and sodium perchlorate. It has been found that acetonitrile is preferentially chemisorbed on the surface either through the non-bonding electrons on the nitrogen atom at potentials positive of the point of zero charge, or on its side in a rehybridized form at negative potentials. The transition between these orientations can be followed by the present technique. The experiments were also used to study the accumulation of solvated cations in the double layer. The spectroscopic data are discussed with respect to the orientation of the solvent and location of the electrolyte ions in the double layer.

Key words: platinum, acetonitrile, adsorption, infrared, electrochemistry.

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INTRODUCTION

The study of the electrochemical behavior of small organic molecules at noble metals constitutes a major part of the research in electrochemical surface science[1]. After early work by Will[2], followed by a sequence of publications by Clavilier[3,4] and other groups[5-7], the underpotential deposition of hydrogen on platinum single crystal electrodes is now understood reasonably well. Furthermore, electrosorption and surface reactivity studies of small organic molecules in aqueous media[8-10] has been shown to be highly sensitive to surface structure.

Nonaqueous solutions have a much wider polarizable potential range than water, an important feature for research in batteries and photoelectrochemical cells[11]. Acetonitrile (AN) is an aprotic solvents whose useful potential range at a platinum electrode is greater than 5 V in tetrabutylammonium tetrafluoroborate solutions[12]. The limiting anodic potential is sometimes hard to define precisely, but it may depend on the purity of electrolyte solution especially with respect to water[13], and electrode pretreatment.

External reflectance infrared spectroscopy has proven to be an invaluable tool for the investigation of the electrode / solution interface[14]. Most experimental work has involved the study of molecular and ionic species adsorbed at the electrode, and therefore, associated with the inner part of the double layer. Our interest has been to use vibrational spectroscopy to study the accumulation of ions in the diffuse part of the double layer. In principal, this is possible for monoatomic ions, especially cations, when these species are solvated by molecules which have IR active vibrational modes.

Although a number of studies of double layer properties for the Hg/non-aqueous solution interface have been carried out[15], very few studies have been made at solid electrodes. This is mainly because the organic solvents must be scrupulously purified in order to obtain reproducible results. Experience in this direction has recently been obtained in our laboratory.

The dependence of interfacial capacitance on potential for tetraethylammonium perchlorate (TEAP)[16-18] and $NaClO_4$[17,18] has been reported for the mercury/acetonitrile interface. No adsorption of tetraethylammonium (TEA^+), Na^+ or ClO_4^- was found over most of the polarizable range of the electrode. The adsorption of AN on polycrystalline[19] and single crystal[20] Pt electrodes from aqueous solutions was also reported. Petrii and Khomchenko[21] investigated the polycrystalline Pt -$LiClO_4$/AN solution interface. On the basis of their data the authors argued that AN is strongly chemisorbed on the Pt electrode.

The purpose of this paper is to describe results obtained at the Pt(hkl)/acetonitrile interface using potential modulated *in situ* reflectance FTIR spectroscopy, also known as subtractively normalized interfacial FTIR spectroscopy (SNIFTIRS). The electrochemical properties of the same system have been studied by measuring the interfacial capacity. The data are analyzed to assess the position of the tetraethylammonium and sodium cations in the double layer and the role of the solvent in determining interfacial structure.

EXPERIMENTAL

Acetonitrile (AN, Aldrich) was purchased as 99.8 % anhydrous and was packed under nitrogen. Tetraethylammonium perchlorate (GFS Chemicals) and sodium perchlorate (Fisher) were purified as described elsewhere[22]. Ferrocene (Aldrich) was used as received. The solutions were prepared in a glove box.

Platinum single crystals with surface orientations (111) and (100) oriented and cut to better than 0.5° were obtained from Metal Crystals and Oxides, Cambridge, UK. The crystals were and polished using standard metallurgical procedures, with a final polishing using 0.05μ alumina. A 10 cm long, 0.7 mm diameter Pt wire was spot welded to the back of the crystal. The wire was pushed through a ceramic tube, 0.6 cm in diameter. After polishing and cleaning for 30 min. in an ultrasonic cleaner, the single crystal was heated in a hydrogen - air flame for 30 min. and quickly transferred into a quartz tube filled with ultra-pure (99.99%) hydrogen. After cooling for 60 seconds a drop of AN was placed on the oriented surface of the electrode, thus preventing it from contamination during transfer to the spectroelectrochemical cell.

All electrochemical and spectroelectrochemical studies were carried out in the cell described below. By employing an attenuated total reflection configuration in conjunction with the reflective surface of platinum electrode, surface plasmon polariton excitation may be established[23]. In order to achieve this, a hard and chemically inert window is necessary. In addition, the angle of incidence should be a few degrees higher than the critical angle θ_c of the window/solution interface which is given by:

$$\theta_c=\sin^{-1}(n_{solution}/n_{window}) \tag{1}$$

where $n_{solution}$ and n_{window} are the refractive indices of the solution and window, respectively. Thus, a material with relatively high refractive index is used. The earlier designs of a thin layer electrochemical cell had a disk or dove prism made of CaF_2 or ZnSe, which comply with above requirements[23-29]. However, most transmission spectrometers have a focusing beam, with ±6° dispersion, so that the angle of incidence is spread over a wide range. Using a hemisphere or hemicylinder, the IR beam can be collimated to achieve an exact angle of incidence.

The cell design and the optical layout are shown in Fig. 1. The cell was made to fit in the external sample chamber of a Mattson RS-1 spectrometer. The focal point of the IR beam is raised upward using a planar gold mirror. The new focal point F_1 is established 2.16 cm from the center of the ZnSe hemisphere, thereby causing the defocusing beam to be collimated throughout the window. In addition, after reflection from the Pt surface, the correct focal point F_2 is reestablished after the beam leaves the hemisphere. The distance d between the focal point and the curved surface of the ZnSe hemisphere is calculated using the simple relationship[30]:

$$d=r/(n-1) \tag{2}$$

where r and n are the radius and refractive index of the hemisphere crystal, respectively. The angle of incidence of collimated IR light is set to 38°.

The cell body was made of Teflon. It has four ports for solution inlet and outlet, a reference electrode port, and a connection for the counter electrode. The reference electrode was a silver wire immersed in a solution of 0.01M $AgClO_4$ with 0.09M TEAP (or $NaClO_4$) in AN. The counter electrode was a Pt wire wound in a loop, placed in a groove of the cell body, and the connection to the solution in the main compartment was made through a glass frit. The working electrode was pressed against the ZnSe crystal by a rubber strap attached to the ceramic tube via a Teflon cap.

During the data collection the solution was blanketed with N_2. Cyclic voltammetry was used to check the state of the electrode surface and cleanliness of the solution before and after each spectrochemical experiment, which could last several hours depending on the number of sample potentials. A custom made potentiostat was used to control the applied potential. Both the spectrometer and the potentiostat were computer-driven. The computer program was written so that the potential of the working electrode was set alternatively to the sample and reference potentials prior to data acquisition. 32 cycles of 128 scans each were coadded, the total number of scans being 4096. The single beam spectrum at the sample potential was ratioed to that at the reference potential, and the data are presented as relative normalized reflectance, $-\Delta R/R$. Thus, a positive going band represents a gain of a particular species at the sample potential relative to that at the reference, whereas a negative going band represents a loss.

Capacitance data were collected by measuring the ac admittance of the interface as a function of dc potential and frequency. The experimental setup and the data analysis were described previously[31]. The concentration of TEAP or $NaClO_4$ for the capacitance measurements was 0.01 M.

All measurements were carried out at 25±0.5 °C. All potentials were normalized and reported with respect to the ferrocene/ferricenium (Fc/Fc^+) redox potential, which was estimated by cyclic voltammetry after addition of ferrocene to the experimental solution.

RESULTS AND DISCUSSION

1. *Cyclic Voltammetry and Capacitance Measurements*

The electrochemical properties of $NaClO_4$ and TEAP in AN were first examined using cyclic voltammetry. No faradaic process was observed in the potential region from -1.2 to +0.8 V against the Fc/Fc^+ couple. At potentials more negative than -1.2 V or more positive than 0.8 V the current starts to rise. Over the time period of the experiments (~24 hrs.) the double layer charging region remains the same, confirming that the system being studied is stable.

Capacitance data collected near the potential of the diffuse layer minimum are shown in Figure 2. Because no indication of specific adsorption of Na^+, TEA^+ or ClO_4^- ions was found in the potential region from -1.2 to 0.8 V, it is assumed that the potential of zero charge (p.z.c.) matches with the minimum on the capacitance curve.

It is known that the work function of single crystal faces increases with atomic density of the crystal plane[32]. Therefore, the work function is expected to be higher for Pt(111) than for Pt(100)[32]. It is predicted that the p.z.c. varies with the crystallographic orientation in the same way[33]. Surprisingly, no dependence of the p.z.c. on crystallographic orientation was found within experimental error (Table 1). Apparently, the chemisorbed AN[21] covers the crystal surface in such a way that the diffuse layer minimum becomes independent of surface crystal structure. Differences in the values of the capacitance at the minimum for different crystal surfaces are assumed to be due to experimental error in determining electrode area rather than to the crystal structure.

The stability of the perchlorate/acetonitrile system has been questioned in a recent paper by Krtil et al.[13]. It was proposed that, at potentials more positive than 2.6 V against the Ag/Ag$^+$ (0.01M) reference (~2.4 V vs. Fc/Fc$^+$), the perchlorate ion is oxidized on the platinum surface, giving the perchlorate radical, which then reacts with acetonitrile, yielding a polyacetonitrile film as the final product[13,34]. Traces of water in the acetonitrile solution are also assumed to catalyze the anodic breakdown of the solvent, although that reaction is not fully understood[13]. However, this instability of the AN system was not reported by other authors, using essentially the same electrolytes. In studies by Pons et al.[12,35-38] a water concentration as high as 0.1M in the tetrabutylammonium tetrafluoroborate system in acetonitrile electrolyte did not result in bands which could be ascribed to the decomposition of acetonitrile, even at positive potentials of 2.5 V against Ag/Ag$^+$ reference[12,38]. However, the band at 2350 cm^{-1}, ascribed to the blue-shifted CN stretch in ref. 35 may be due instead to an asymmetric stretching mode in CO_2 formed on the electrode surface[13].

2. *Transmission Spectra*

Figure 3 shows IR transmission spectra of acetonitrile (neat liquid) and of 0.1M solutions of tetraethylammonium perchlorate and $NaClO_4$. Pure acetonitrile (Fig. 3a) shows the following bands (in cm^{-1}): 3163 [$\nu(C\equiv N)+\nu(C-C)$], 3003, 2945 [$\nu(C-H)$], 2293 [$\nu(C-C)+\delta(C-H)$], 2253 [$\nu(C\equiv N)$], 1444, 1375 [$\delta(C-H)$], 1041 [$r(C-H)$], 918 [$\nu(C-C)$] and 748 where ν is a stretching mode, δ, a deformation mode, and r, a rocking vibration. These frequencies agree with those reported in other sources[13,39-41]. The C≡N stretching frequency and the combination band $\nu(C-C)+\delta(C-H)$, as well as $\nu(C-C)$ and $\delta(C-C\equiv N)$ overtone are sensitive to the presence of cations in the solution[42-44]. They shift to the blue to an extent which is proportional to the charge/radius ratio. New solvent bands, due to acetonitrile molecules in solvation shell of sodium cations appear at 2299, 2265, 923 and 761 cm^{-1}[44] and can be observed in Fig. 3c as shoulders on the corresponding free AN bands. In the TEAP solutions (Fig 3b), there is no measurable shift of these bands.

3. *SNIFTIRS Measurements in TEAP Solutions*

Fig. 4 shows SNIFTIR spectra obtained in the TEAP/AN solutions for Pt(100). The reference potential E_r was kept at -0.25 V against Fc/Fc^+ and the sample spectra were recorded at more negative potentials. Other than the bands at 2363 and 2340 cm^{-1}, which could be due to the changes of CO_2 concentration in the IR optical path, two positive going bands at 2293 and 2253 cm^{-1} in Fig. 4a are clearly visible. Since the AN molecules in the solvation shell of TEA$^+$ cation cannot be distinguished from the free AN by their IR bands (c.f. Fig. 3), the positive going features could result from the concentration change of either free acetonitrile, or the acetonitrile solvating the TEA$^+$ cation at the interface. Accumulation of TEA$^+$ ions occurs because the negatively charged Pt(100) surface attracts the positively charged TEA$^+$ cations into the double layer. However, a comparison with the spectra for Pt(111) in TEAP/AN, as well as the data for the $NaClO_4$/AN system reveals that accumulation of free AN molecules is also possible, as is explained further below. We conclude that the increase in reflectivity of the two bands probably arises as a result of both processes.

The broad bipolar band with a negative lobe at ~2160 cm^{-1} and a positive one at ~2060 cm^{-1} is sensitive to the electrode potential, and therefore could be associated with AN adsorbed on the platinum surface. In recent publications[20,45] it has been proposed that AN is chemisorbed at the surface in either a donative state, through the lone electron pair on the nitrogen atom (state I), or associative state, in which both the carbon and the nitrogen atoms are bonded to platinum surface (state II), as shown in Fig. 5.

Hubbard et al.[45] reported that immersion of Pt(111) into liquid AN at open circuit produces a chemisorbed layer of AN in state I with the $\nu(C\equiv N)$ band at 2150 cm^{-1}, as observed in a high resolution electron energy loss spectrum (HREELS). Therefore, the negative going lobe of the bipolar band observed in Fig. 4a could be due to the change of orientation of AN at the electrode surface. At potentials negative to p.z.c., an adsorption state through the lone electron pair seems less probable than state II (see Fig. 5). However, since the ν(C=N) band of acetonitrile adsorbed on the surface in state II cannot be observed in a SNIFTIR spectrum with perpendicularly polarized light, the potential induced reorientation of the AN from adsorption state I to state II could be followed only by the changes in the C-C and C-H vibrational modes. SNIFTIR spectra in the region 1450~700 cm^{-1} show that all the bands that correspond to the AN, as well as the perchlorate stretching band at 1100 cm^{-1}, are negative-going. From the above adsorption models, it is obvious that all oscillators in state I interact more strongly with the surface electric field than in adsorption state II, so that the reorientation from I to II produces negative-going bands in the $-\Delta R/R$ spectrum, as observed in Fig. 4b.

SNIFTIR spectra of AN adsorbed on Pt(111) at negative potentials are shown in Fig. 6. The behavior of all the bands is similar to that observed in Fig. 4. This similarity is somewhat surprising, since the adsorption of AN from aqueous acidic solutions is believed to be surface dependent, as shown by cyclic voltammetry[20]. However, these changes are based on hydrogen adsorption on the sites not occupied by AN, and therefore give little insight regarding the sites on which AN adsorbs. Furthermore, the stability of AN in the presence of water even at open circuit is still not completely understood[45]. On the other hand, the capacitance data shown in Fig. 2 suggest strong chemisorption of AN at platinum electrodes, thus suppressing effects due to the differences in surface structure.

The similarity of the spectra shown in Figs. 4 and 6 leads to the conclusion that anhydrous AN adsorbs on different platinum surfaces at identical adsorption sites, that is, either on top of one platinum atom or between two neighboring Pt atoms. At negative electrode potentials the latter seems more probable. As a result, one AN molecule interacts with two platinum atoms, as would be the case in adsorption state II. If the platinum electrode is covered with the acetonitrile adsorbed in state I at potentials positive to p.z.c. (as in the case of the background potential at -0.2 V), reorientation from I to II at more negative potentials causes some AN molecules to desorb from the surface. This reorientation produces the positive going bands observed in the 2550~1850 cm^{-1} region in Figs. 4a and 6a. This could be another reason for the observed increase in the reflectance at 2253 and 2293 cm^{-1}.

Adsorption of AN at positive potentials on polycrystalline platinum and gold surfaces has been studied by several groups[12,29,35-38]. It was concluded earlier[12,29] that the chemisorbed AN has a C≡N stretching band at 2342 cm^{-1}. However, this band coincides with dissolved CO_2[46]. It has been shown that the reaction of AN with perchlorate at positive potentials higher than 2.2 V against the SCE yields CO_2 as the main oxidation product[13]. Therefore, in this work we have chosen a positive limit at which no measurable faradaic process takes place, as confirmed by cyclic voltammetry. Figs. 7 and 8 show spectroelectrochemical data for the two platinum crystals in 0.1M TEAP/AN solution at potentials from 0.45 to 0.75 V against Fc/Fc^+. Since the data for the two crystals are similar further discussion considers their common behavior. A summary of the main SNIFTIRS bands in TEAP/AN system is reported in Table II.

In the 2550~1850 cm^{-1} region, Figs. 7a and 8a, two major positive going bands at 2304 and 2272 cm^{-1} are clearly visible. They are attributed to AN strongly chemisorbed on Pt(hkl) to an extent which increases as the electrode potential is made more positive. A blue shift in the C≡N stretching frequency is expected, as discussed by several authors[12,13,29,35-38]. However, it should be noted that it is not nearly as big as reported in some studies[12,29]. The origin of the broad bipolar band between 2200 and 2000 cm^{-1}, which is also observed at negative sample potentials, is still unclear. It is noteworthy that this band has been observed in both aqueous[29] and nonaqueous solutions[13], but no assignments have been offered.

A comparison of the negative going bands at 2253 and 2293 cm^{-1} observed in Figs. 7a and 8a with the transmission spectra in Fig. 3 reveals that the former correspond to either free AN, or AN solvating the TEA$^+$ cation. In order to clarify this further, the spectral features in the range 1450~700 cm^{-1} in Figs. 7b and 8b were inspected. Bands due to the TEA$^+$ cation at 1190, 1174, 1000 and 785 cm^{-1} are all negative going, suggesting that these species leave the double layer together with AN in the solvation shell. On the other hand, the positive going bands of AN at 1037, 918 and 754 cm^{-1} suggest that a transition from adsorption state II to I occurs. AN is preferentially adsorbed in state I at potentials positive of the p.z.c., as argued earlier[29].

A close inspection of the spectral features at 918 and 754 cm^{-1} in Fig. 3b shows that the bands are both sharp and not affected by the presence of the TEA$^+$ cation. However, in the spectrum of the $NaClO_4$/AN solution, Fig. 3c, these bands are split, the higher energy mode being attributed to the presence of Na$^+$[44]. Therefore, it is reasonable to suppose that the influence of the positively charged electrode surface on the shift of these bands would be similar. Figs. 7b and 8b show that the spectral manifold near 920 cm^{-1} can be resolved into two bands, centered at 928 and 918 cm^{-1}. These two resolved bands correspond to the ν(C-C) stretching frequencies of adsorbed AN molecules and free AN, respectively. Therefore, the ν(C-C) of adsorbed AN is shifted by 10 cm^{-1} to the blue.

The spectral feature centered at 760 cm^{-1} is also composed of two bands, but its profile is distorted by the presence of the negative-going TEA^+ band at 785 cm^{-1}. It has been shown earlier[44] that the shift of ν(C-C) is, to a first approximation, equal to one-half of the ν(C≡N) shift. Therefore, the ν(C≡N) band of adsorbed AN should be about 20 cm^{-1} shifted to the blue. This provides another confirmation that the 2272 cm^{-1} band represents the strengthened ν(C≡N) vibration.

4. *SNIFTIRS Measurements in $NaClO_4$ Solutions*

The experimental data obtained by SNIFTIRS in $NaClO_4$/AN solutions on the two single crystal surfaces are shown in Figs. 9 and 10. At negative potentials, two positive bands at 2290 and 2254 cm^{-1} appear in the 2550~1850 cm^{-1} region, together with negative bands at 2265 and 2298 cm^{-1} at Pt(100), see Fig. 9a. Similar bands are observed at Pt(111), Fig. 10a. Since the sodium cation shifts the frequency of the combination and the C≡N stretching bands of the AN molecules in its solvation shell by 5 and 13 cm^{-1} to the blue, the observed increase in reflectance of the non - shifted bands at 2290 and 2254 cm^{-1} can be correlated only to the concentration change of free acetonitrile at the interface. The free acetonitrile molecules can be produced by the transition from the adsorption state I into II, as explained above. However, they can also be produced partly by the destruction of the solvation shell of Na^+ cations, as explained below.

It is reasonable to assume that the concentration of sodium ions in the double layer at potentials negative to the p.z.c is higher than at the reference potential. Therefore, the concentration of AN molecules in the double layer due to the solvation shells of sodium cations is also higher, and consequently positive going bands at 2264 and 2298 cm^{-1} are expected. However, the opposite is observed in the spectra shown in Figs. 9 and 10. This result can be due to some destruction of the solvation shell of sodium cations in the vicinity of the negatively charged electrode which, in turn, may be a result of underpotential deposition (UPD) of Na$^+$ on the platinum surface. It has been reported that the UPD peak potential of Na$^+$ on Pt in propylene carbonate is -1.53 V against the SCE, that is, about -1.72 V against Fc/Fc$^+$[47]. Although the onset of UPD was not reported, it could be inferred from Fig. 1 in ref. 47 to be around -1.3 V against Fc/Fc$^+$; this result agrees with our observations.

At positive potentials several peaks are visible (see Table III). The peaks at 2305 and 2273 cm^{-1} are attributed to AN adsorbed on the well oriented platinum surface, as discussed above. In addition, the loss of free acetonitrile molecules in the double layer is visible from the negative going bands at 2293 and 2256 cm^{-1}. The spectra also show two additional positive going bands at 2318 and 2285 cm^{-1}. A careful comparison of Figs. 9a and 10a with Figs. 7a and 8a reveals that these bands are also present in the data for the TEAP/AN system as small shoulders. The origin of these bands is not clear. However, it is possible that they represent the adsorption of AN on step sites formed during the positive potential step, as discussed below.

It is well known that the anodic excursion of polycrystalline platinum in aqueous media beyond 0.6 V vs. SCE leads to surface oxidation, with the formation of HOPt in which platinum atoms irreversibly exchange place with hydroxyl groups[48]. Atomically flat surfaces of platinum single crystals are also prone to this "turnover" process, which results in the formation of steps. It is possible that traces of water in acetonitrile act as a catalyst for surface oxidation. Therefore, adsorption of acetonitrile in a subsequent positive potential step can proceed on step sites formed in this manner as well as on true terrace sites. Since the charge density on step sites is higher relative to the terrace sites, the AN adsorbed on steps should have bands shifted to higher wavenumbers. Single crystal stepped surfaces with different step densities should be used in future experiments in order to confirm this conclusion. However, it should be noted that the bands at 2318 and 2285 cm^{-1} are more pronounced in the spectrum for Pt(100) than in that for Pt(111). It is known that the Pt(111) surface is much more stable to surface oxidation that Pt(100)[5]. Also, these bands are more pronounced in $NaClO_4$/AN than in the TEAP/AN system. This could be due to the fact that the $NaClO_4$ salt is more hydroscopic than TEAP, and, although the salts were dried extensively under vacuum, the water content in the $NaClO_4$/AN solutions is probably higher. Higher water content may lead to a higher density of steps formed in the positive potential step, and consequently to a higher concentration of AN adsorbed on step sites.

In the 1450~700 cm^{-1} region of Figs. 9b and 10b, at potentials negative of the p.z.c. all AN bands, together with the ν_3 (ClO_4^-) are negative going. The loss of reflectance at 1043, 921 and 757 cm^{-1} can be correlated to the destruction of the solvation shell of the Na^+ cations. The 1100 cm^{-1} band corresponds to perchlorate ions being repelled from the double layer. At positive potentials, the perchlorate band is positive going, due to the concentration increase of negatively charged ions in the double layer. Also, the r(C-H) band at 1043 cm^{-1} is positive going. A careful inspection of the envelope close to 930 cm^{-1} reveals that it is composed of a negative band centered at 918 cm^{-1} corresponding to the loss of free AN, and two positive bands at 938 and 928 cm^{-1} which probably correspond to the C-C stretching frequency for AN adsorbed on steps and terraces, respectively.

In conclusion, the present study demonstrates the ability of *in situ* reflectance infrared spectroscopy to investigate the structure of the double layer. This is realized by following the IR bands of free solvent molecules, as well as those adsorbed at the electrode surface and in the solvation shell of ions in the electrolyte during the potential modulation. The obtained results clearly show that there is a distinct difference among the IR characteristics of each type of molecule. Also, there is an indication that the solvent molecules are sensitive to the microscopic surface structure, showing the influence of steps and terraces on the IR band shift. Experimental results dealing with a study of acetonitrile adsorbed on platinum and gold stepped surfaces will be presented in a future paper.

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Table I: Potentials of zero charge on the ferrocene/ferricenium scale for the interface Pt(hkl)/AN with 0.01 M TEAP or $NaClO_4$ as electrolyte at 25 °C.

electrolyte	p.z.c.$_{(Fc)}$ Pt(100)[a]	p.z.c.$_{(Fc)}$ Pt(111)[a]
TEAP	-0.51	-0.51
$NaClO_4$	-0.49	-0.50

[a] error ±0.01 V

Table II. Overview of the main SNIFTIRS bands in the 2550-700 cm^{-1} region for platinum single crystals in 0.1M TEAP/AN and assignments. All assignments refer to acetonitrile molecules, unless stated otherwise.

Negative potentials				Positive potentials			
Positive bands		Negative bands		Positive bands		Negative bands	
cm^{-1}	Assignment	cm^{-1}	Assignment	cm^{-1}	Assignment	cm^{-1}	Assignment
2342	CO_2 dissolv.	1375	δ C-H	2304	comb.[a] ads.[c]	2363	CO_2 (gas)
2290	comb.[a]	1100	ν_3 ClO_4^-	2272	ν C≡N ads.[c]	2338	CO_2 (gas)
2253	ν C≡N	1037	r C-H	1099	ν_3 ClO_4^-	2293	comb.[a] free
		918	ν C-C	1037	r C-H	2253	ν C≡N free
		754	δ C–C≡N ovt.[b]	928	ν C-C ads.[c]	1190, 1174	TEA^+
				918	ν C-C	1000	TEA^+
						785	TEA^+

[a] combination band, ν(C-C)+ δ(C-H)

[b] overtone

[c] AN adsorbed through lone electron pair on nitrogen (state I in Fig. 5)

Table III. Overview of the main SNIFTIRS bands in the 2550-700 cm^{-1} region for platinum single crystals in 0.1M $NaClO_4$/AN and assignments. All assignments refer to acetonitrile molecules, unless stated otherwise.

Negative potentials				Positive potentials			
Positive bands		Negative bands		Positive bands		Negative bands	
cm^{-1}	Assignment	cm^{-1}	Assignment	cm^{-1}	Assignment	cm^{-1}	Assignment
2363	CO_2 (gas)	2298	comb. solv.	2318	comb. ads. step	2293	comb. free
2340	CO_2 (gas)	2265	ν C≡N solv.	2305	comb. ads. terr.	2256	ν C≡N free
2290	comb.[a] free	1100	ν_3 ClO_4^-	2285	ν C≡N ads.step	918	ν C-C free
2254	ν C≡N free	1043	r C-H	2273	ν C≡N ads.terr.		
		921	ν C-C solv.	1043	r C-H		
		757	ovt.[b] solv.	938	ν C-C ads. step		
				928	ν C-C ads. terr.		
				757	δ C–C≡N ovt.[b]		

[a] combination band, ν(C-C)+ δ(C-H)

[b] δ C–C≡N overtone

solv. - AN in solvation shell

ads. terr. - AN adsorbed on terrace sites (true Pt(hkl) sites)

ads. step - AN adsorbed on step sites formed on Pt(hkl) during previous positive excursion

FIGURE CAPTIONS

Figure 1. SNIFTIRS cell used in the study. 1) The Teflon cell body, 2) ceramic tube with platinum wire pushed through it, 3) reference electrode port, 4) single crystal electrode, 5) gold mirrors, 6) ZnSe hemisphere, 7) counter electrode port. F_1 and F_2 - focal points of the incident and reflected beams, respectively. The ports for inlet and outlet of solution are omitted for clarity.

Figure 2. Capacitance of Pt(111) and Pt(100) in 10 mM solutions of (a) TEAP/AN and (b) $NaClO_4$/AN at 25 °C as a function of electrode potential against Fc/Fc^+.

Figure 3. Transmission IR spectra of: (a) neat AN, (b) 1M solutions of TEAP in AN, and (c) 1M solution of $NaClO_4$ in AN in 2550~1850 and 1450~700 cm^{-1} region.

Figure 4. SNIFTIR spectra in the 2550~1850 (a) and 1450~700 cm^{-1} region (b) obtained for Pt(100) in a 0.1M TEAP/AN solution as a function of electrode potential. Sample potentials were taken every 100 mV, starting from -0.95 V (top curve) to -1.25 V, with background scan taken at -0.25 V against Fc/Fc^+. 4096 scans were coadded, with 4 cm^{-1} resolution.

Figure 5. Models for adsorbed CH_3CN through the lone electron pairs (I) and on its side, bonded through a rehybridized C=N bond (II).

Figure 6. SNIFTIR spectra in 2550~1850 (a) and 1450~700 cm^{-1} region (b) obtained for Pt(111) in 0.1M TEAP/AN solution as a function of electrode potential. Sample potentials were taken every 100 mV, starting from -0.7 V (top curve) to -1.2 V,

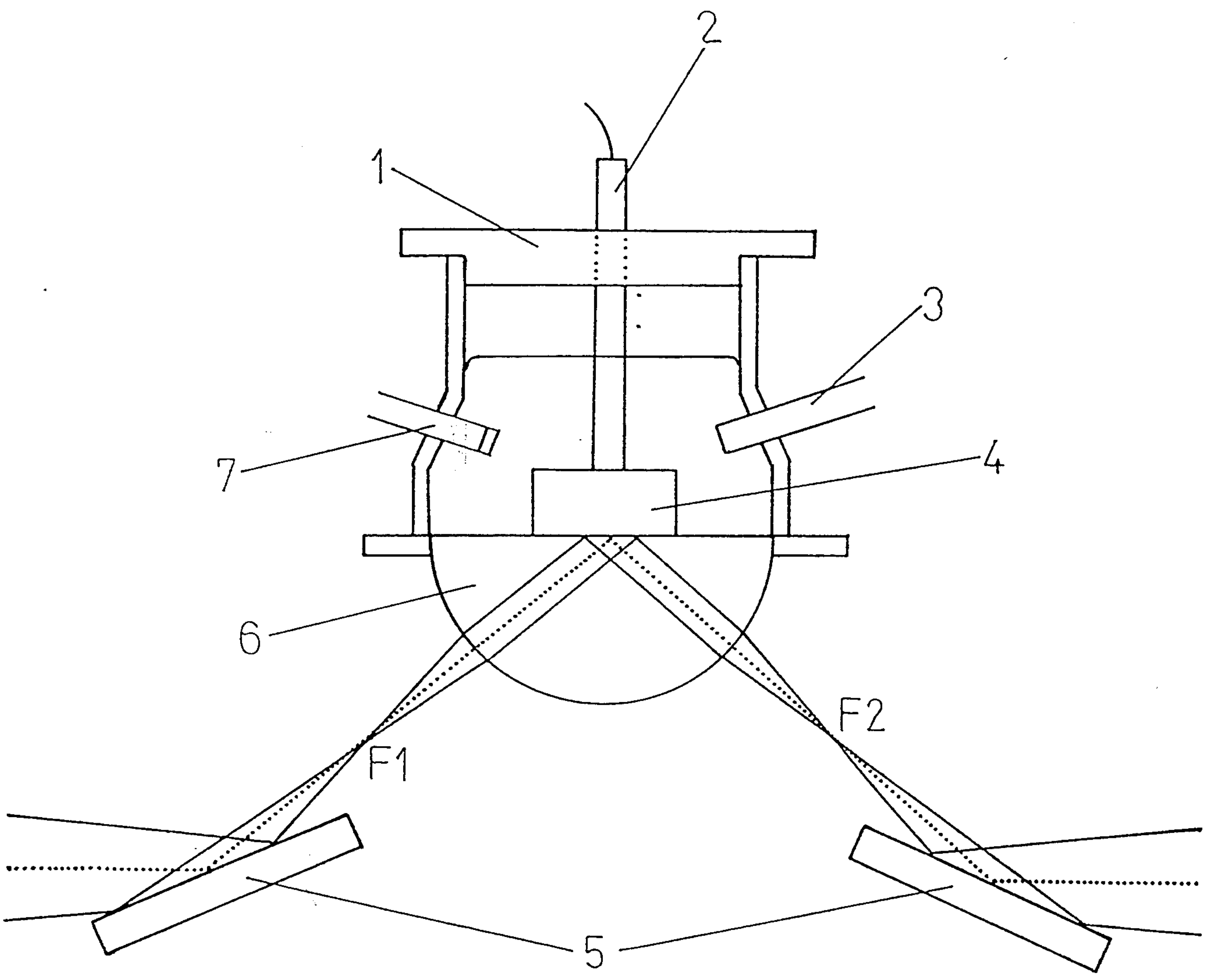
with background scan taken at -0.2 V against Fc/Fc$^+$. 4096 scans were coadded, with 4 cm^{-1} resolution.

Figure 7. SNIFTIR spectra in 2550~1850 (a) and 1450~700 cm^{-1} region (b) obtained for Pt(100) in 0.1M TEAP/AN solution as a function of electrode potential. Sample potentials were taken every 100 mV, starting from 0.45 V (bottom curve) to 0.75 V, with background scan taken at -0.25 V against Fc/Fc$^+$. 4096 scans were coadded, with 4 cm^{-1} resolution.

Figure 8. SNIFTIR spectra in 2550~1850 (a) and 1450~700 cm^{-1} region (b) obtained for Pt(111) in 0.1M TEAP/AN solution as a function of electrode potential. Sample potentials were taken every 100 mV, starting from 0.3 V (bottom curve) to 0.8 V, with background scan taken at -0.2 V against Fc/Fc$^+$. 4096 scans were coadded, with 4 cm^{-1} resolution.

Figure 9. SNIFTIR spectra in 2550~1850 (a) and 1450~700 cm^{-1} region (b) obtained for Pt(100) in 0.1M $NaClO_4$/AN solution as a function of electrode potential. Sample potentials were taken every 400 mV, starting from 0.8 V (top curve) to -1.2 V, with background scan taken at 0.2 V against Fc/Fc$^+$. 4096 scans were coadded, with 4 cm^{-1} resolution.

Figure 10. SNIFTIR spectra in 2550~1850 (a) and 1450~700 cm^{-1} region (b) obtained for Pt(111) in 0.1M $NaClO_4$/AN solution as a function of electrode potential. Sample potentials were taken every 400 mV, starting from 0.8 V (top curve) to -1.2 V, with background scan taken at 0.2 V against Fc/Fc$^+$. 4096 scans were coadded, with 4 cm^{-1} resolution.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F2
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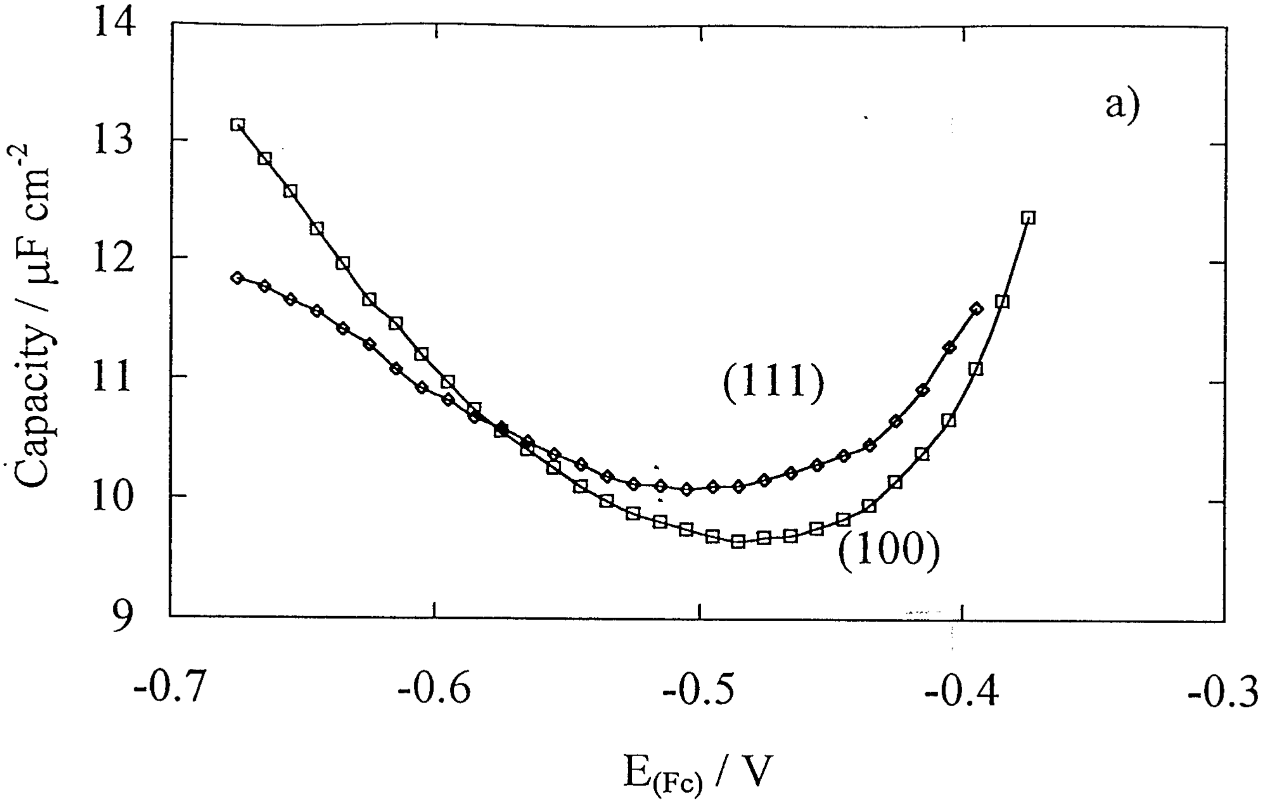
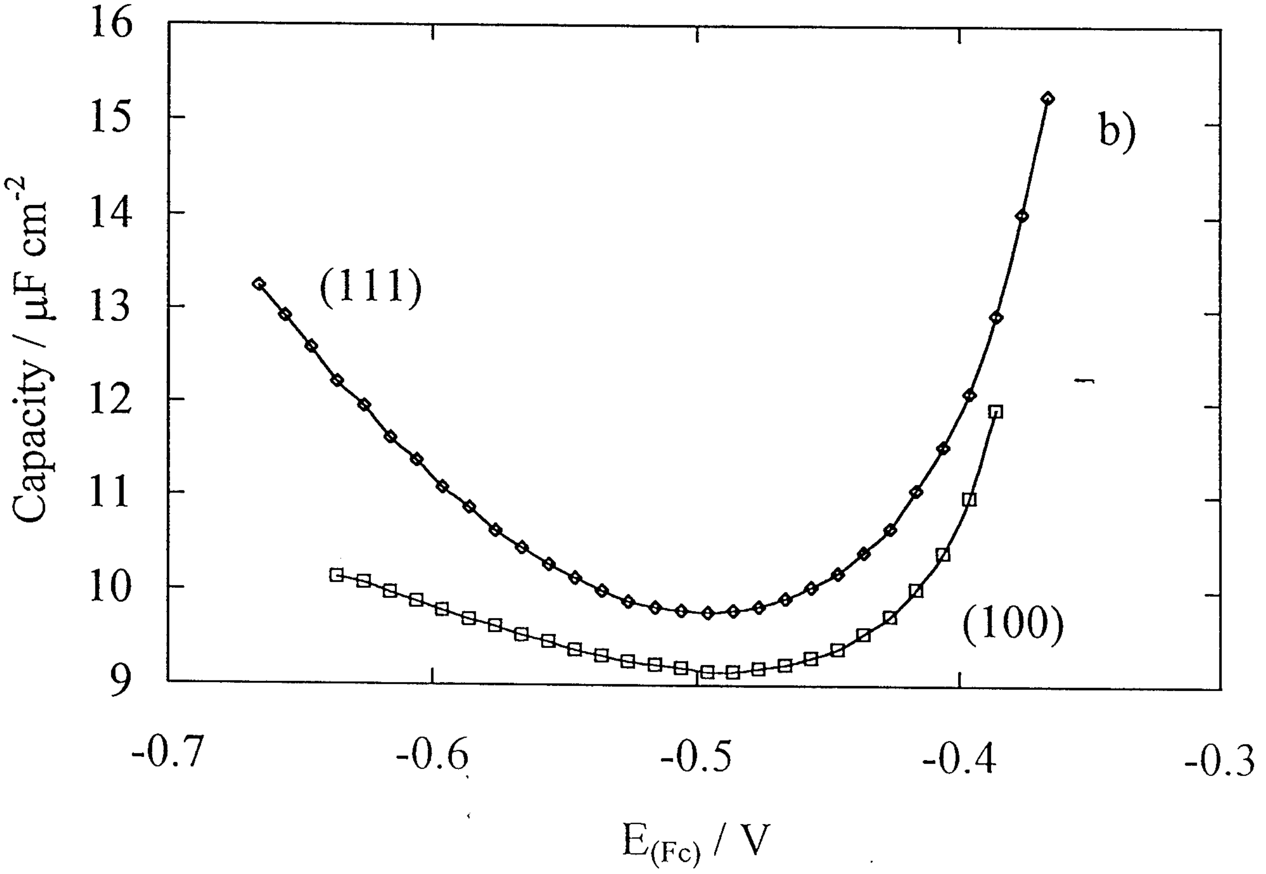
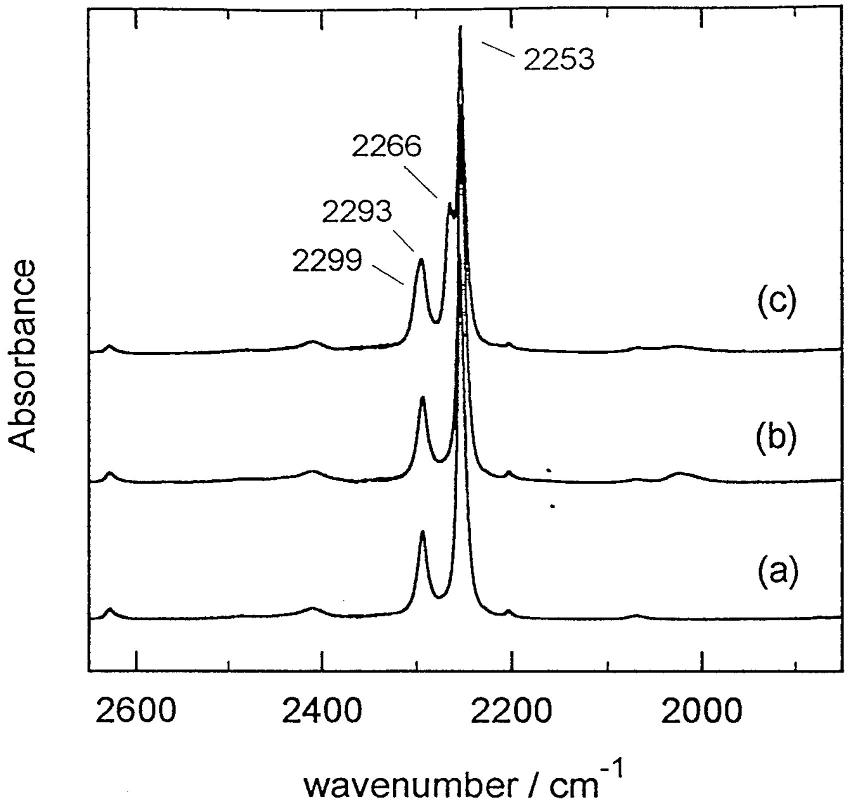
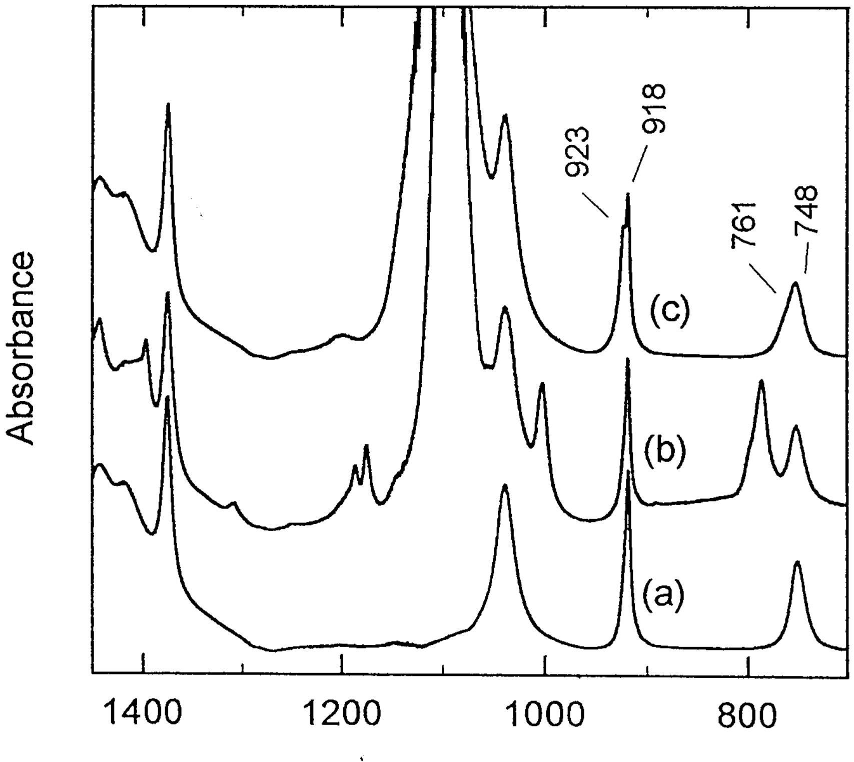

a)
(111)
(100)
Capacity / µF cm-2
14
13
12
11
10
9
-0.7
-0.6
-0.5
-0.4
-0.3
E(Fc) / V

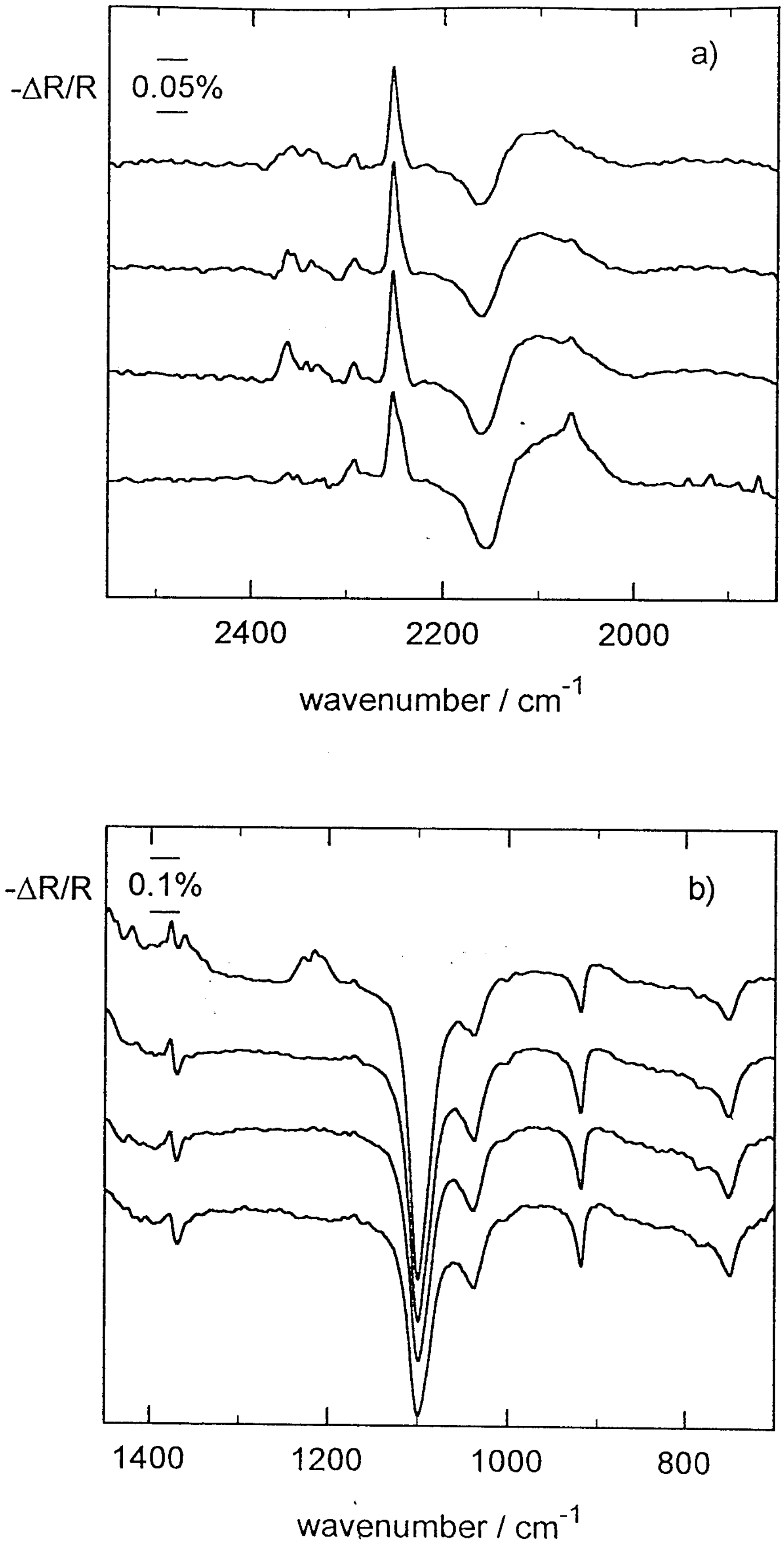

b)
(111)
(100)
Capacity / µF cm-2
16
15
14
13
12
11
10
9
-0.7
-0.6
-0.5
-0.4
-0.3
E(Fc) / V

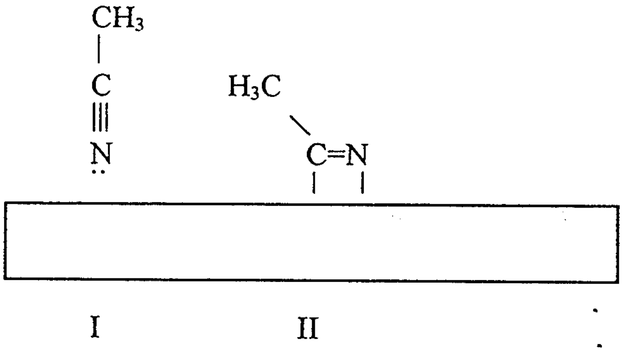


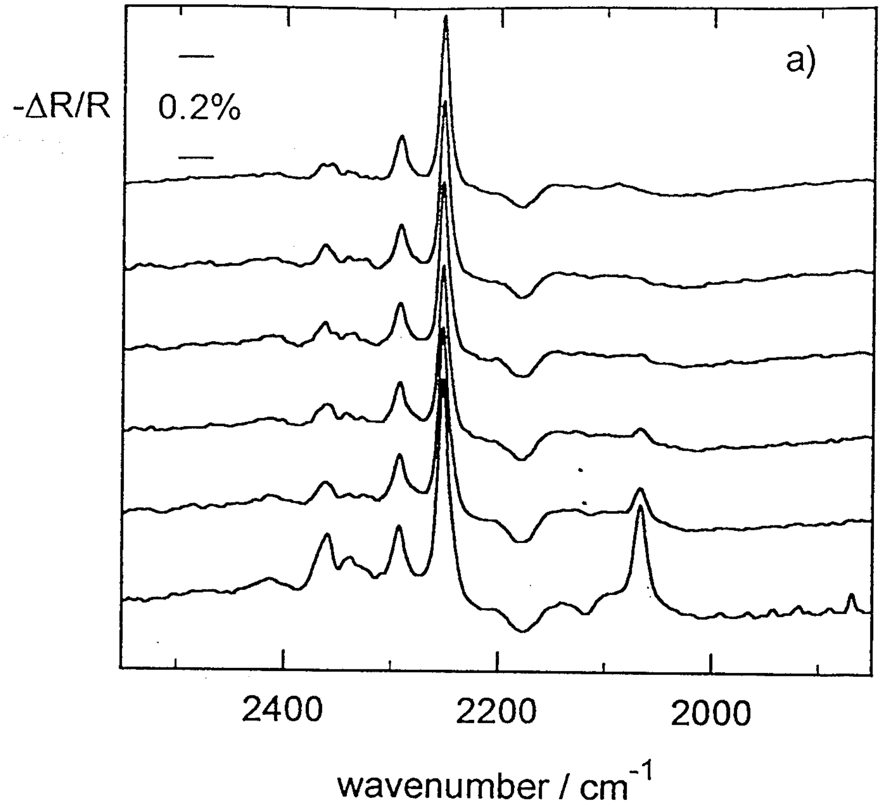
2253
2266
2293
2299
(c)
(b)
(a)
Absorbance
2600
2400
2200
2000
wavenumber / cm-1



923
918
761
748
(c)
(b)
(a)
Absorbance
1400
1200
1000
800
wavenumber / cm-1


-ΔR/R
0.05%
a)
2400
2200
2000
wavenumber / cm^{-1}
-ΔR/R
0.1%
b)
1400
1200
1000
800
wavenumber / cm^{-1}


CH3
C
N
H3C
C=N
I
II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0.2%
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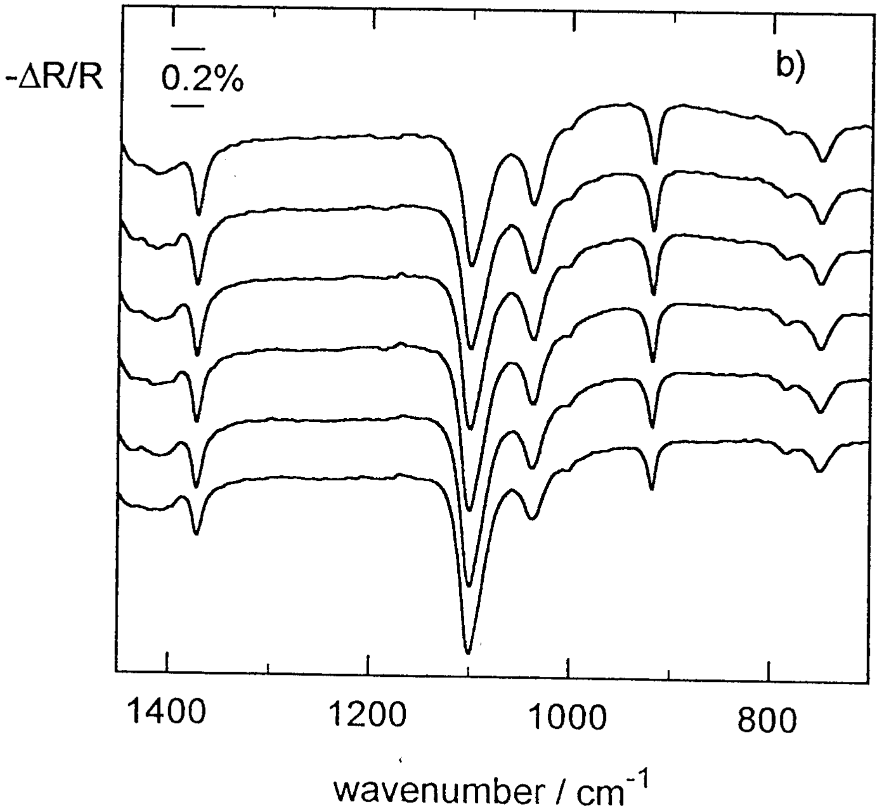
2200
2000
wavenumber / cm-1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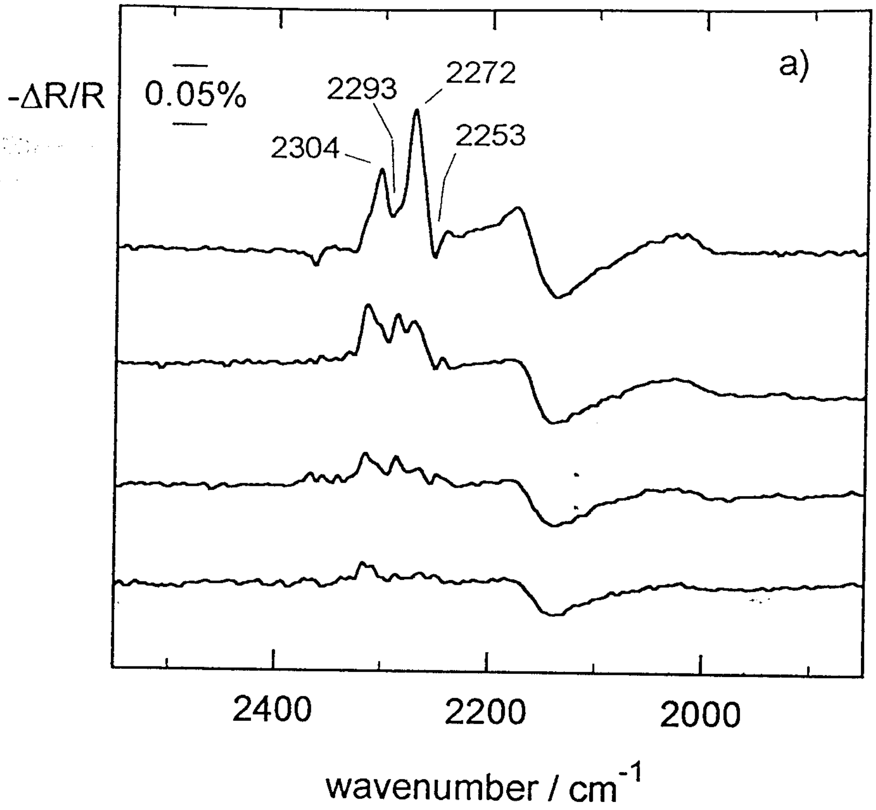
0.2%
1400
1200
1000
800
wavenumber / cm-1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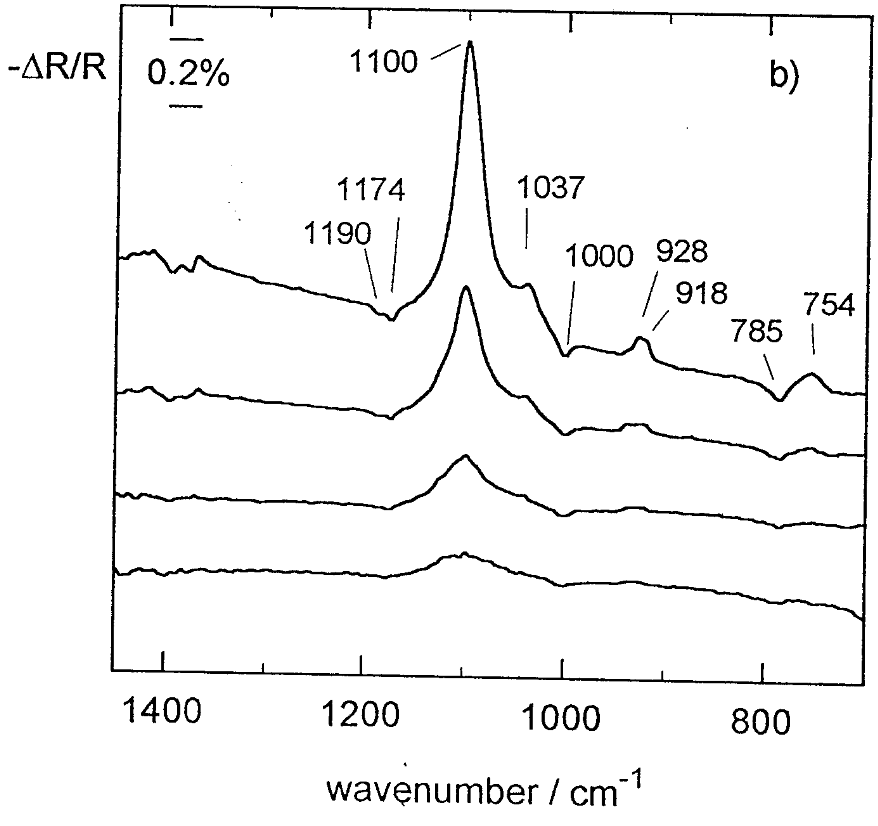
0.05%
a)
2293
2272
2304
2253
2400
2200
2000
wavenumber / cm-1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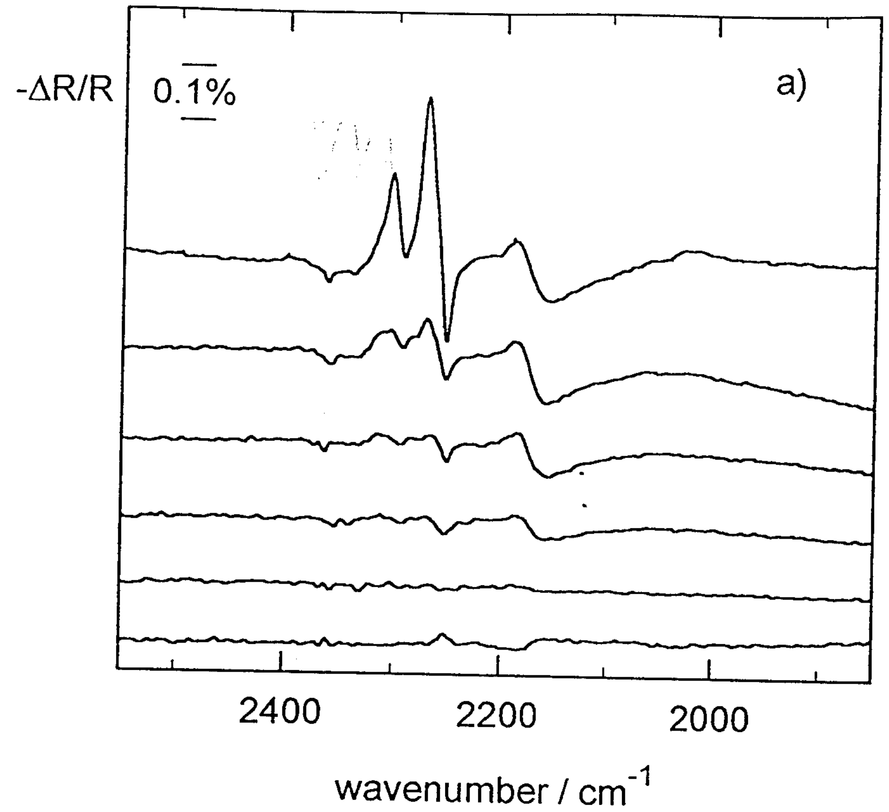
0.2%
1100
b)
1174
1037
1190
1000
928
918
785
754
1400
1200
1000
800
wavenumber / cm-1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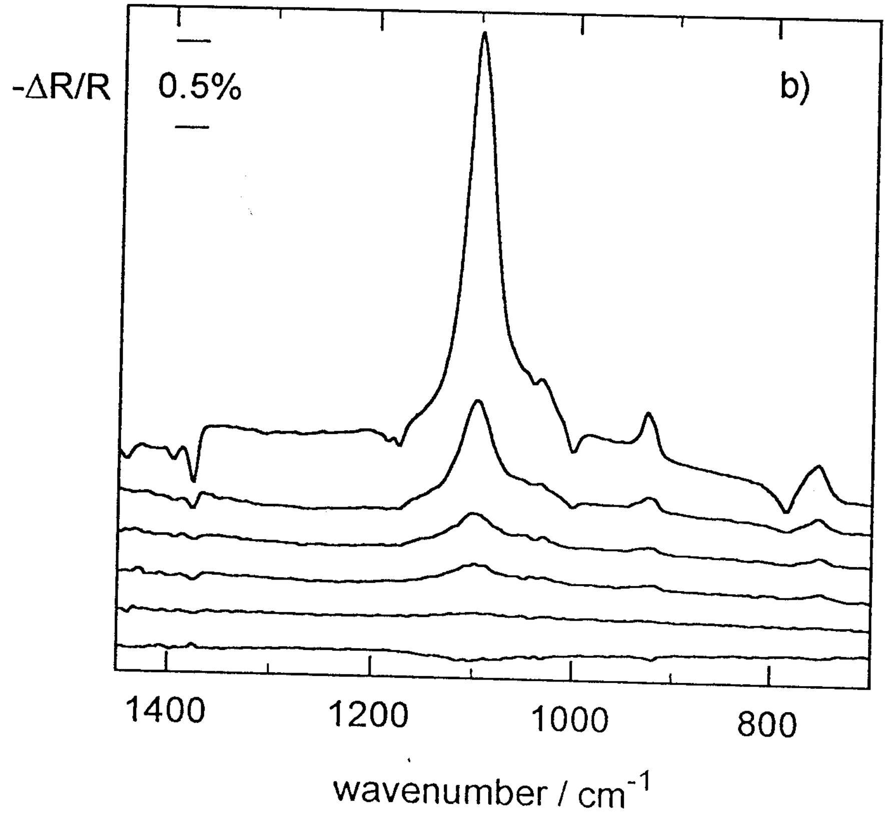
2200
2000
wavenumber / cm-1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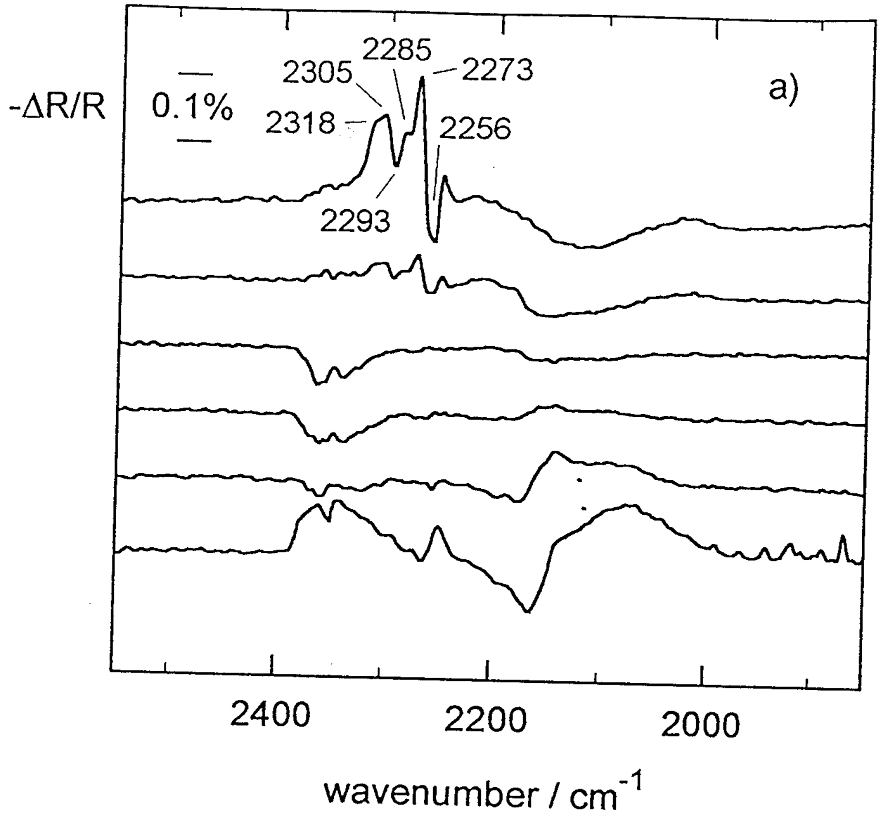
1000
800
wavenumber / cm-1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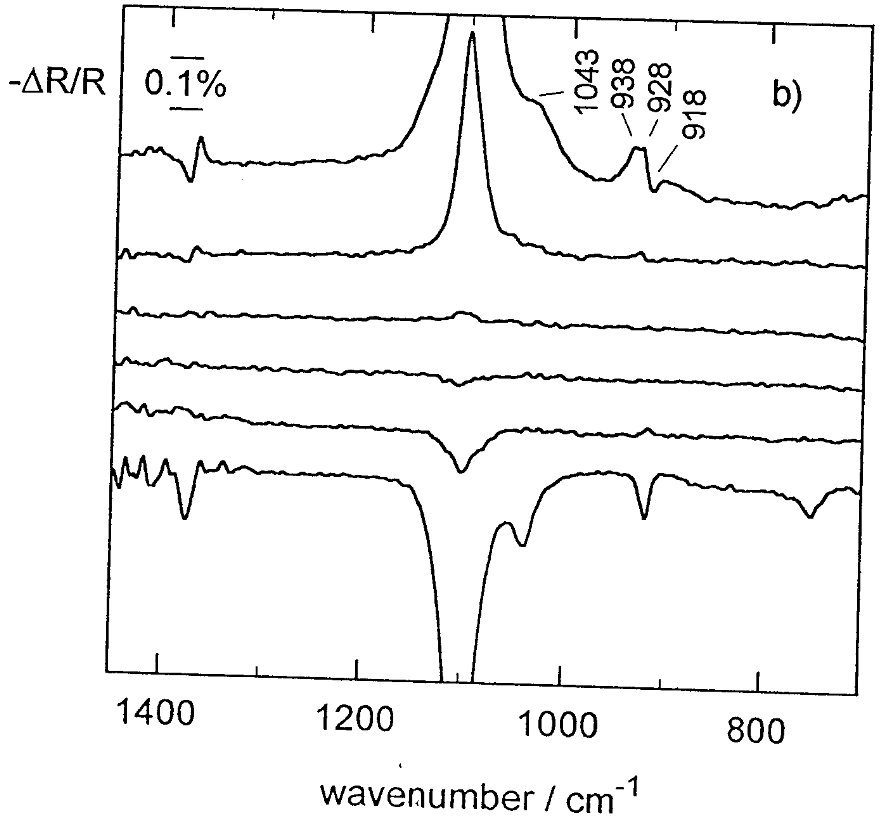
2305
2285
2273
a)
2318
2256
2293
2400
2200
2000
wavenumber / cm-1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938
928
918
b)
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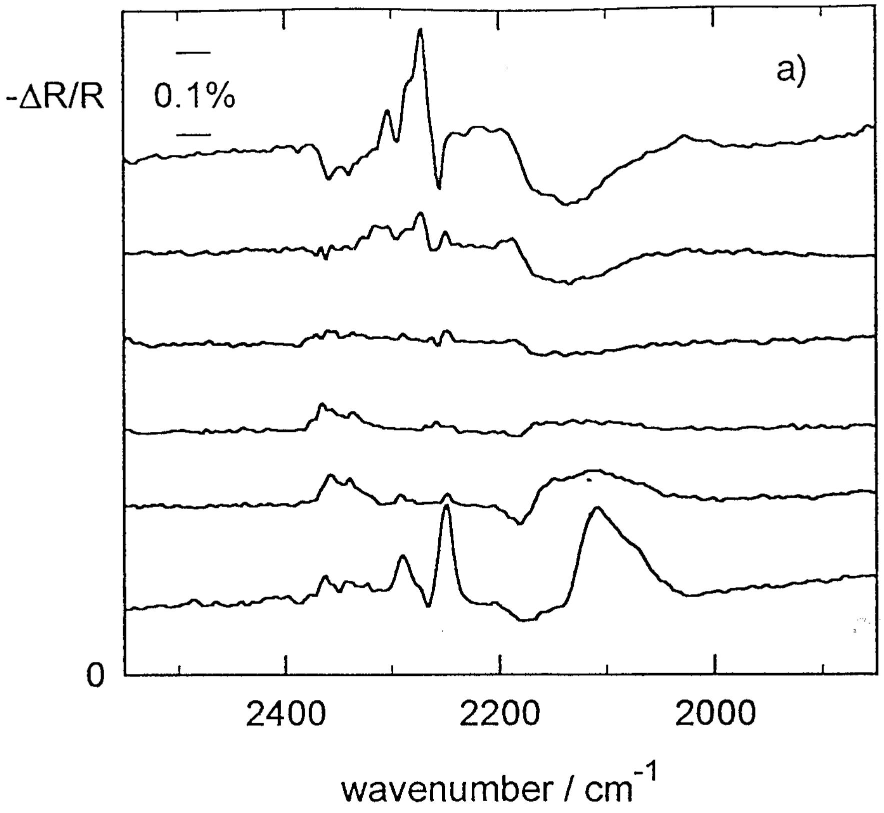
1200
1000
800
wavenumber / cm-1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a)
0
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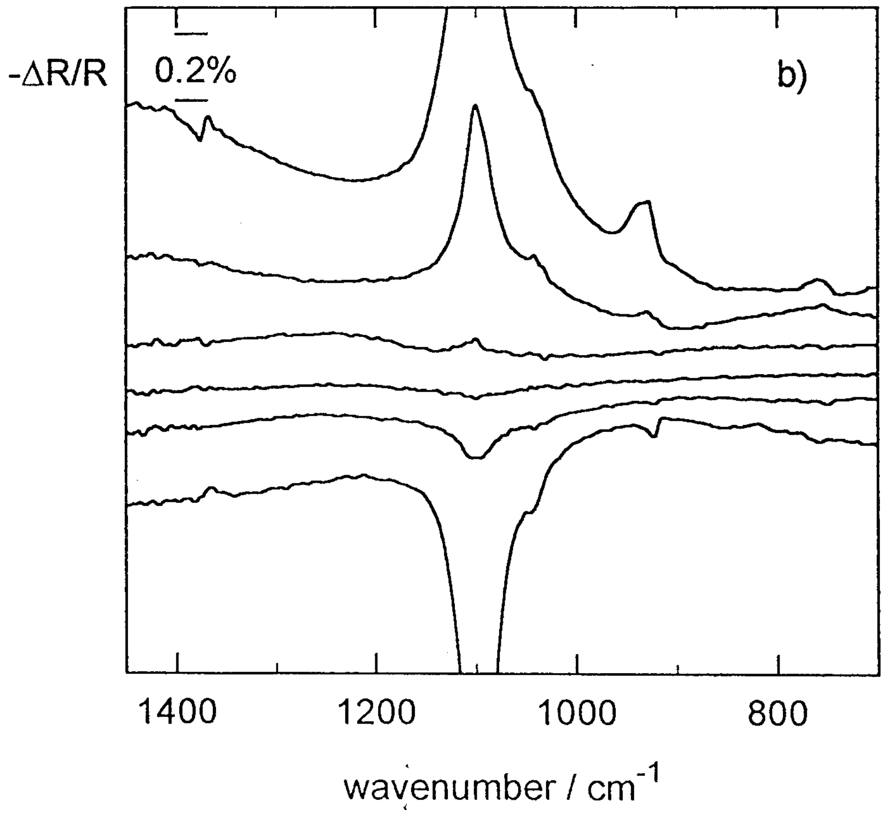
2200
2000
wavenumber / cm^{-1}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wavenumber / cm^{-1}