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Enhancement and band distortion of the IR absorption spectra of a methanol on silver evaporated thin films in UHV-ATR configuration

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Abstract. Enhanced infrared absorption spectra of methanol adsorbed on evaporated silver films were measured using Kretschmann's ATR configuration. Whereas the enhanced spectra were recordable using p-polarized radiation alone when the metal film was continuous, it was obtainable using both the p-polarized and s-polarized radiations from island films. Band distortion was also measured for changing incident angle and metal thickness. Furthermore, when film with silver of intermediate thickness was used, great distortion of the absorption band was observed. The relation between the anomalous absorption by the silver film and the band distortion was indicated.

PACS. 78.30.-j Infrared and Raman spectra

1 Introduction

Hartstein et al. [1] and later Hatta et al. [2–4] found that infrared absorption of molecules adsorbed on evaporated silver or gold films were enhanced one or two orders of magnitude using Kretschmann's ATR configuration [5].The ATR method was used because it had been inferred that infrared absorption enhancement resulted from excitation of surface plasmon polariton (SPP). However, subsequent research clarified that the enhancement mechanism does not depend on excitation of SPP [6,7]. In fact, an absorption increase occurred even when the transmission method was used [8,9]. The ATR method has a defect in that the optical system configuration becomes complicated in comparison with the transmission method. For that reason, the transmission method became the emphasis of subsequent research.

Difficulties in obtaining reproducible results on the metal-induced enhancement are concerned mainly with substrate surface contamination. Contamination not only influences the metal films' morphology. It also disturbs their morphological inspection in the scanning electron microscope. The requirement of clean surfaces has led us to prepare fresh silver films under UHV conditions followed by exposure to physisorbing gaseous molecules [8,9]. In the transmission experiment in UHV, many valuable observation results were obtained in clarifying the absorption enhancement mechanism.

This progress has come about because the transmission configuration, a simple optical system, is used. On the other hand, the ATR method has an important advantage aside from SPP excitability. Some examples are the existence of the electric field vector in the direction normal to the interface and a probe light does not pass through a sample film. These cannot be obtained by the transmission method.

The multiple reflection ATR method using a fixed angle of incidence demands only a comparatively simple optical system: there are none of the many difficulties attending in situ measurement in UHV.

Wadayama et al. performed in situ measurement in UHV using the multiple reflection ATR method [10].

Especially, the angle resolved ATR method using a single reflection type prism is an outstanding method offering the features shown below by changing the incidence angle.

(1) The strength ratios of the electric field vectors in parallel and vertical directions are changeable.
(2) Penetration depth changes. Consequently, it has spatial resolution in the depth direction of a sample.
(3) By bringing an incidence angle close to a critical angle, it is possible to enlarge the parallel electric field vector about four times that of the penetration method case.

However, as stated previously, a complicated optical system is required to use the angle resolved ATR method. It was difficult to use a complicated optical system with the UHV system. Therefore, ATR measurement in UHV has not been performed until now. Moreover, the infrared absorption enhancement spectrum using a free electron metal thin film is often accompanied by great absorption-band distortion [11]. Nevertheless, the cause of that

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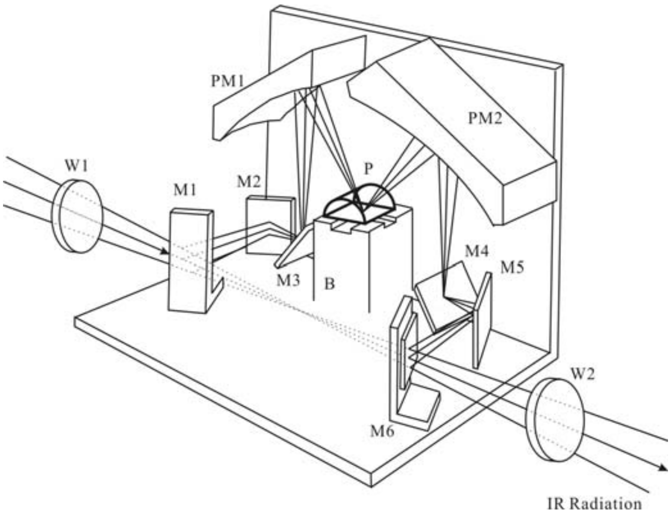


Fig. 1. Schematic drawing of angular resolved ATR optics for in situ UHV infrared measurement. M1–M6: plane mirror, PM1–PM2: paraboloidal mirror, P: ATR prism, B: cooling base for sample, W1–W2: IR transparent window.

distortion remains unclear. Furthermore, the mutual relation of distortion and absorption increases remains unresolved.

This study conducts an experiment that uses angle resolved ATR configuration in UHV; in addition, we explore the relation between the infrared absorption enhancement phenomenon and absorption band distortion.

2 Experimental

Infrared measurements using the Kretschmann configuration were performed using the SEAGULL® (Harrick Scientific Products Inc.). SEAGULLL cannot be used for UHV because it is equipment used in the atmosphere. We altered the device by providing oil-free lubrication to the sliding components. The base plate was newly designed and the handle was remodeled for changing the beam incidence angle on the sample for application to UHV measurement. Figure 1 shows a schematic drawing of the SEAGULL® with the ATR prism used in this work. Thin silver films of desired thickness were deposited at a rate of 1 nm/min on a reflection plane of a hemicylindrical Ge prism at room temperature by electron-beam evaporation in a vacuum chamber evacuated to 5×10^{-10} Torr. Afterward, each silver film was cooled to 120 K and exposed immediately to methanol. Silver-films thicknesses were evaluated using the frequency changes of a quartz crystal oscillator placed adjacent to the prism, taking the density of the silver films as equal to that of the bulk density.

The infrared radiation was incident on the totally reflecting Ge prism/Ag film interface at angles of incidence of 20–70°. Infrared absorption spectra were obtained using an FTIR spectrophotometer (MB-100; ABB Bomem) with an average of 64 scans at 4 cm^{-1} resolution.

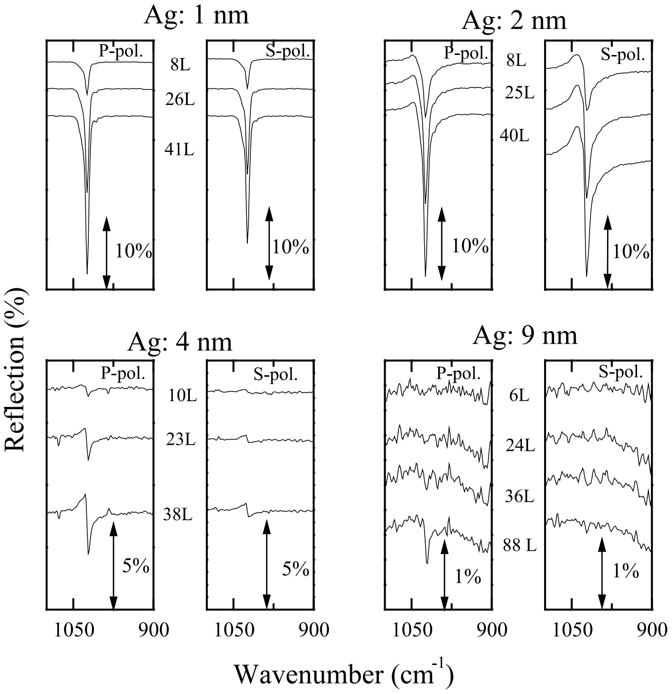


Fig. 2. Polarized ATR Spectra for methanol adsorbed at 120 K on silver films with the indicated thicknesses taken at an angle of 60°.

3 Results and discussion

Figure 2 shows the infrared absorption enhanced ATR spectra of methanol adsorbed on silver films obtained at a 60° angle of incidence. Thickness of the silver film is 1–9 nm and the amount of methanol exposure is displayed in the figure. The amount of the introduction was evaluated using Langmuir (L, 1 $L = 10^{-6}$ Torr × 1 s). The spectra exhibit a band at 1025 cm^{-1} attributable to the C–O stretch of methanol. Absorption intensity increases with respect to ATR experiment without metal film, but as soon as the metal film thickness increases, the absorption intensity decreases. Moreover, when the silver film thicknesses were 1 and 2 nm, the absorption intensity was nearly independent of the polarization state of radiation. However, when a silver film of 4 nm in thickness was used, the absorption intensity by s-polarization decreased remarkably; when a silver film of 9 nm thickness was used, the infrared spectrum was only enhanced by p-polarized radiation. These features correspond approximately to the observation results in the atmosphere [3]. Moreover, they are similar to the measured results in the atmosphere: distortion is observed to the absorption band of methanol when an intermediate-thickness silver film is used [11]. The band distortion is explained later.

It is difficult to determine the exact absorption intensity because the band is distorted. However, to evaluate it roughly, the peak to peak measurement shows the absorption intensity. The amount plotted to the amount of introduction is shown in Figure 3. The dotted line in the figure shows the result for cases in which silver does not exist (normal ATR). In the case of 2 nm, the enhancement

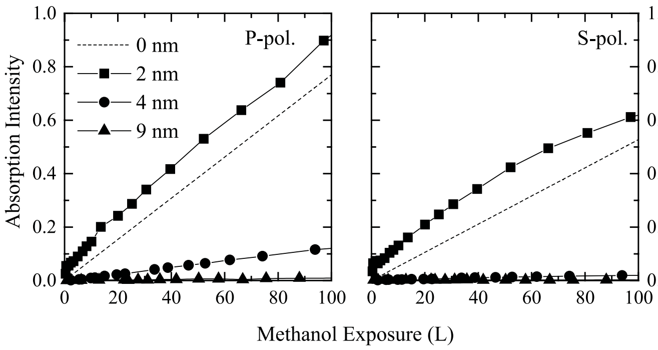


Fig. 3. Absorption intensity of the methanol C–O stretch mode as a function of methanol exposure. The methanol was deposited at 120 K on the indicated thicknesses of silver.

factor was greater than one, but for the cases of 4 and 9 nm, it was less than one.

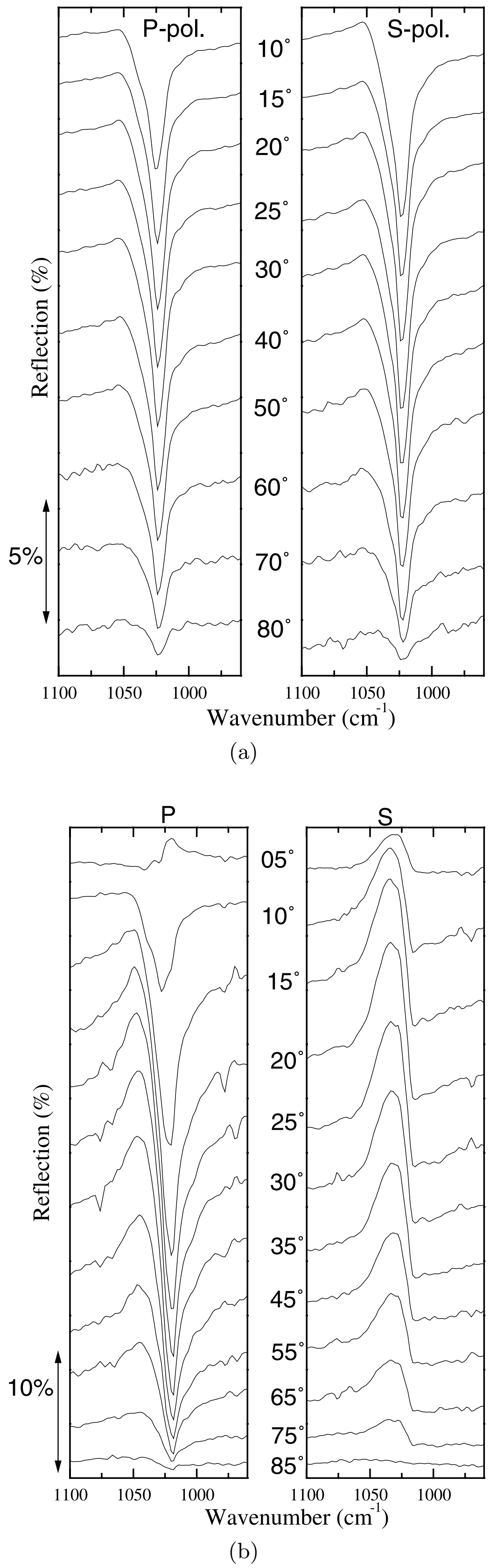
Next, the angle resolved infrared ATR spectrum of methanol adsorbed on a silver thin film is shown in Figure 4. The film thickness of a silver thin film is 1.9 and 3.6 nm; and the amounts of methanol exposure are 3.5 and 3.8 *L*, respectively.

The focus of IR radiation shifted from the ideal. Therefore, the width of the incidence angle is a little large. Although it comes out, the incidence angle dependability appears clearly. The incidence angle and polarization dependences on absorption intensity and band distortion are not contradictory to the measurement result in the atmosphere [3]. These confirm that in-situ UHV-ATR is realizable.

A particularly remarkable band distortion appeared in the result of 3.6 nm. Past measurements [11] show that when large distortions appeared, absorption intensity was inferred to be small. Evaluation of absorption intensity was difficult because of band distortion, but if it is evaluated using peak to peak measurements, absorption intensity is inferred to be very strong in the case of 3.6 nm. This inference differs considerably from results obtained heretofore.

Figure 5 shows the incidence angle dependence of absorption intensity. The sample reflectivity is also plotted in this figure. We confirmed that reflectivity decreases in inverse proportion to the absorption intensity, just as it did in studies that had been done in atmosphere in the past [6]. It was also clarified that band distortion is observed not only in bulk samples, such as in liquid methanol, but in a thin film sample as it was this time.

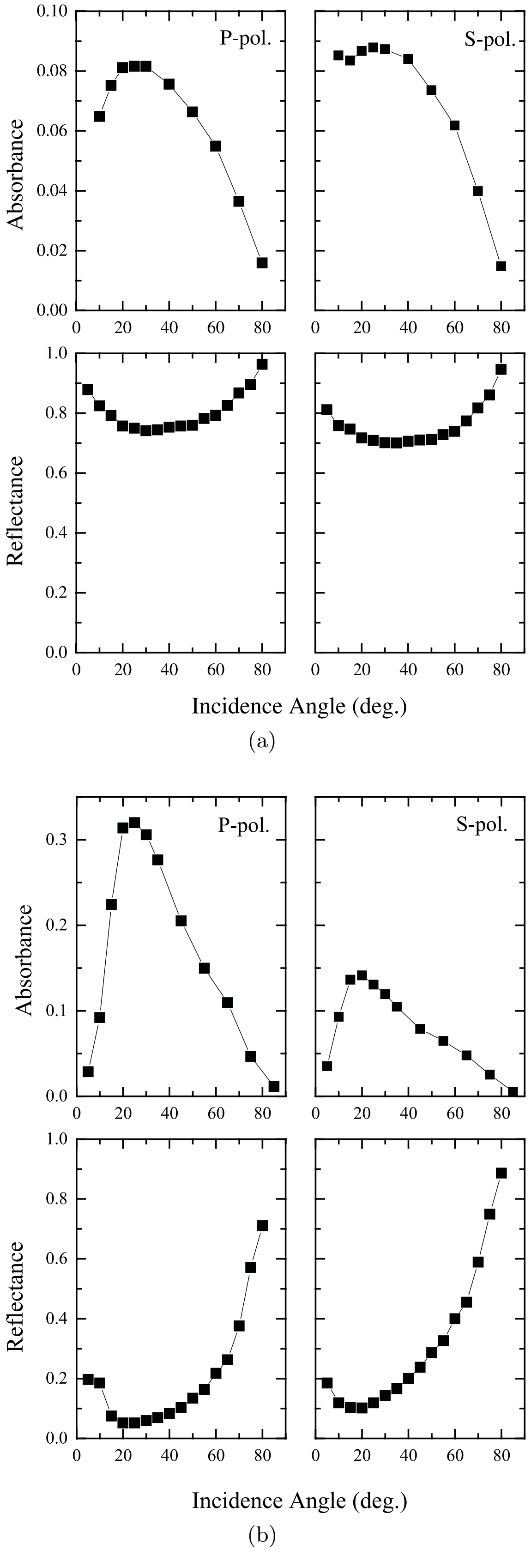
Figure 2 shows a remarkable band distortion observed for 4 nm films when p-polarized radiation is used. However, the band distortion is not evident in 6 and 9 nm films. On the other hand, when s-polarized radiation is used, band distortion is already evident in the 2 nm film, and a remarkable distortion is observed in the 4 nm film. As mentioned above, for comparatively thick films (6 and 9 nm), these results agree with results of past research: the absorption band is not observed [3].



(a)

(b)

Fig. 4. Polarized ATR Spectra for methanol adsorbed at 120 K on silver films, measured as a function of the angle of incidence. (a) 1.9 nm, 3.5 *L*; (b) 3.6 nm, 3.8 *L*.



(a)

(b)

Fig. 5. Variation of absorbance of the methanol CO stretch mode and reflectance at 1025 cm^{-1}. (a) 1.9 nm, 3.5 L; (b) 3.6 nm, 3.8 L.

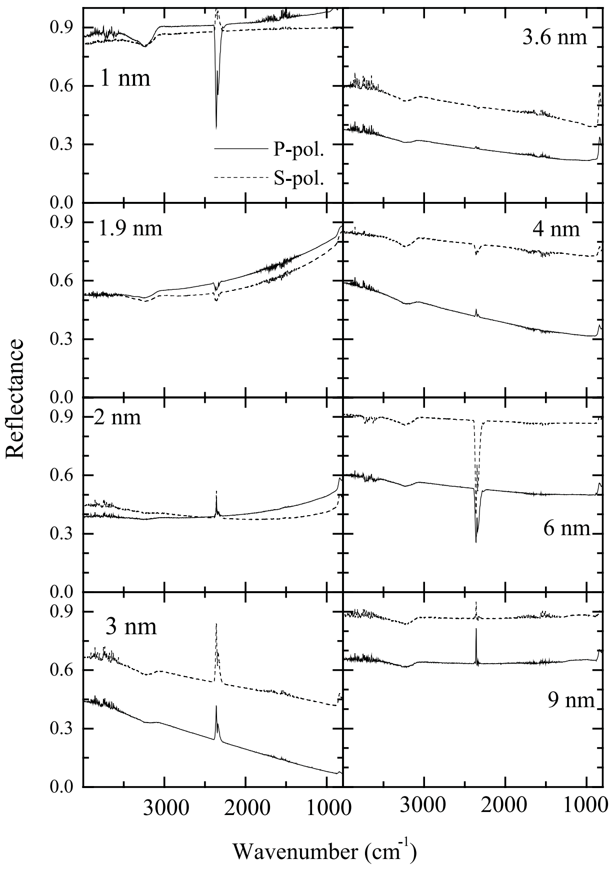


Fig. 6. Reflectance change with respect to the bare Ge prism with the indicated thicknesses taken at an angle of 60°.

Reflectivity

As mentioned above, to investigate why film thickness, by which distortion of an absorption peak is observed, differs by p-polarization and s-polarization, we devote our attention to reflectivity. Reflectivity measurements were performed in UHV condition. Figure 6 depicts the silver film thickness dependence of infrared reflectance. The silver film thickness is 1 to 9 nm. Each reflectivity value was normalized with respect to the reflectivity of the bare germanium prism. The band at 2350 cm^{-1} is assigned to atmospheric $\mathrm{CO_2}$ molecules; the bands at 4000–3500 cm^{-1}, 3200 cm^{-1}, and 1800–1300 cm^{-1} are assigned to atmospheric water vapor molecules in the optical path. Reflectance decreases once and increases thereafter when both polarizations are used with the increase in film thickness. The overall inclination of reflectance should be carefully noted here. Although reflectance decreases with the increase in wavenumber in 1 and 1.9 nm films, reflectance decreases by the low wavenumber side conversely for 3 to 6 nm films. The wavenumber dependence of reflectance changes with film thickness based on the influence of surface scattering and anomalous absorption by the metal film: it is considered to originate in film percolation [12]. Reflectivity decreases concomitant with the decrease in wavenumber if the metal's dielectric constant is considered. However, reflectivity on the high wavenumber side is lower in a thin film thickness because the influence of surface scattering is great. The influence of surface dispersion is large if a film is a discontinuous island film. The influence of surface scattering will become small if a film grows as a continuous film. Thereby, the film has grown to be a continuous film from an island film at about 2 nm, which influences its surface scattering reflectivity and reverses anomalous absorption. Reflectance is almost flat at thickness of 9 nm just because the influence of anomalous absorption weakens and silver begins to show its character not as a thin film, but as a bulk material.

Reflectivity and distortion of the band

A difference exists also in the wavenumber dependence of reflectivity by p-polarization and s-polarization when 2 nm is viewed. That point shows a difference in the existence of the band distortion by each polarization. For p-polarization, although the reflectance is high by the side of the low wavenumber, for s-polarization, the result is reversed. This fact indicates that the influence of surface scattering is large when p-polarization is used; the influence of the anomalous absorption by a film is large when s-polarization is used. The relation between wavenumber dependence of reflectivity and band distortion shows the following things.

(1) Band distortion does not occur when the influence of surface scattering by a film is strong.
(2) A band is distorted when anomalous absorption by a metal film is strong.

Band distortion occurs only when the influence of the anomalous absorption by a film is strong. Therefore, the absorption band distortion is inferred to depend strongly on anomalous absorption by a film.

Next, we consider the silver-film-thickness dependence of infrared absorption intensity. When the silver film is thin, its absorption intensity is a little large. It does not have a great difference arising from polarization, either. Great absorption was obtained near the percolation threshold, especially when p-polarization was used. Moreover, the absorption band was markedly distorted and absorption band reversal was evident in the case where s-polarization was used. In addition, when a thick silver film was used, weak infrared absorption was observed only for the case in which p-polarization was used. The intensity in this case was 1/10 or less than that for the case in which a thin silver film was used. These results are similar to results of atmospheric measurements, as reported earlier [3].

We must give particular attention to another important matter. As shown in Figures 2 and 6, absorption band distortion is observed in cases of exposure to great amounts of methanol. Pucci et al. reported distortion of an absorption band about CO on Fe [13]. In this case, because only monolayer adsorption takes place, the model of occurrence of absorption band distortion holds that it arises from interaction between metal and adsorbed CO. However, the present study confirmed that absorption band distortion occurs, just as it does for molecules that do not directly adsorb on metal. A new model is therefore required to explain absorption band distortion.

4 Summary

A clear relation between the infrared absorption enhancement phenomena in infrared spectroscopy using free electron metal and absorption band distortion like that observed in these cases does not exist. Moreover, the cause of band distortion has not been resolved. This study observed infrared absorption enhancement of a methanol exposed on evaporated silver films of various thicknesses. Distortion of an absorption band was not observed when silver film thickness was 1 nm. Absorption band distortion reached its highest value when the silver film thickness was about 4 nm. However, at silver film thickness of 9 nm or greater, the absorption band distortion was not observed. Moreover, it became clear that the film thickness by which distortion of a band is observed differs in cases of p-polarization and s-polarization. Then, we considered which is more dominant in band distortion — surface scattering or anomalous absorption. Results elucidated that the band distortion occurs when the effect of anomalous absorption by the film is predominant. This inference is supported by the lack of observation of band distortion in films with the dominant effect of surface scattering and in films without anomalous absorption. Furthermore, we confirmed that the silver-film-thickness dependence of infrared absorption intensity in a UHV system shows the same tendency as results in the atmosphere.

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