

Intensity Enhancement in Infrared ATR Spectra of 1-Monolayer LB Films of Stearic Acid by Various Evaporated Metal Films

Toshihide KAMATA*, Junzo UMEMURA*, and Tohru TAKENAKA*

Received August 10, 1987

Intensity enhancements in infrared ATR spectra of 1-monolayer LB films of stearic acid with evaporated Pt, Cu, Ni, and Al overlayers was investigated by Fourier transform infrared spectroscopy. Including the same data on Ag and Au overlayers reported previously [T. Kamata, A. Kato, J. Umemura, and T. Takenaka, *Langmuir*, to be published; T. Kamata, J. Umemura, and T. Takenaka, *Bull. Inst. Chem. Res., Kyoto Univ.*, **65**, 170 (1987)], the intensity enhancement factors for the asymmetric CH_3 stretching band in the range of metal film thickness from 0 to 3 nm were found to be in the order $\text{Au} > \text{Ag} > \text{Pt} \approx \text{Cu} > \text{Ni} > \text{Al}$. The origin of this order was discussed in terms of the complex dielectric constant and liability to oxidation of each metal. The enhancement factors by these metals other than Au and Ag were so small that they were not suited for the practical purpose of high sensitivity infrared ATR measurements.

KEY WORDS: FT-IR ATR spectra/ Stearic acid/ Langmuir-Blodgett film/
Intensity enhancement/ Pt Cu Ni Al metals

INTRODUCTION

In previous works,^{1,2)} we have studied intensity enhancements in infrared ATR spectra of Langmuir-Blodgett (LB) films of stearic acid overcoated with evaporated Ag or Au films. Some differences have been found between the effects of Ag and Au films. For example, the intensity enhancement factor for each absorption band by the Au film was roughly twice as large as that by the Ag film when the metal film thickness was the same. Such differences may originate from those in physicochemical properties such as dielectric constant between Ag and Au. In the case of surface enhanced Raman scattering (SERS), which also result from the interaction between electromagnetic waves and adsorbed molecules on metal surfaces,³⁾ many investigations have been performed on these problems.⁴⁻¹⁰⁾ Concerning intensity enhancements in infrared ATR spectra, on the other hand, there is only one paper¹¹⁾ which has dealt with the effect of various metals on polymer band intensities, as far as we know. Therefore, it is worthwhile to investigate the metal dependence of infrared ATR spectra of LB films, not only from the theoretical point of view but also for the practical purpose. The use of LB films has several advantages such as the good contact to the ATR prism and the ample informations on the molecular orientation and film thickness.

In the present work, we expanded the study of this series^{1,2)} to evaporated Pt, Cu, Ni, and Al films, and the intensity enhancement factors for the CH stretching bands of 1-monolayer LB films of stearic acid were compared among these metals.

* 鎌田俊英, 梅村純三, 竹中 亨: Laboratory of Surface Chemistry, Institute for Chemical Research, Kyoto University, Uji, Kyoto-Fu 611.

EXPERIMENTAL

Details of the deposition of the 1-monolayer LB film of stearic acid on the Ge ATR prism have been described previously.^{1,12)}

Shapes, purities, and sources of evaporation metals are as follows. Cu: Chip, 99.9% purity, Nakarai Chemicals, Ltd., Pt: wire of 0.1 mm diameter, 99.99% purity, Oken Trade Co., Ni: wire of 0.125 mm diameter, 99.9% purity, Japan Lamp Industries Co., Ltd., and Al: wire of 0.5 mm diameter, 99.999% purity, Japan Lamp Industries Co., Ltd.. As evaporation sources, we used a tungsten wire for Pt, a tungsten filament for Al, and tungsten boats for Cu and Ni. Metal films with mass thicknesses of 0.5–4 nm were evaporated on one large face of the Ge prism with a 1-monolayer LB film of stearic acid in an Ulvac Model EBH-6 vacuum evaporator at 3×10^{-6} Torr. The rate of evaporation was 6 nm min^{-1} except for Pt for which 0.6 nm min^{-1} was adopted. The rate of evaporation and mass thickness of the metal films were evaluated by an Ulvac Model CRTM deposition monitor equipped with an oscillating quartz crystal.

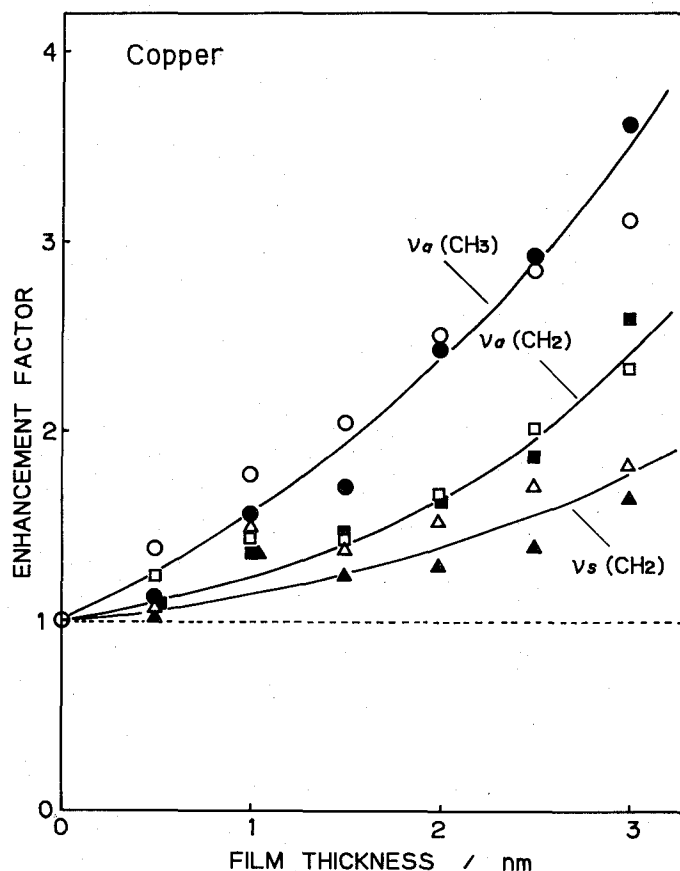


Fig. 1. Intensity enhancement factors for the CH stretching bands of 1-monolayer LB films of stearic acid as functions of Cu film thickness. Open and solid symbols refer to p- and s-polarized radiations, respectively.

Polarized infrared ATR measurements were performed by a Nicolet Model 6000C FT-IR spectrophotometer equipped with an MCT detector. Details of the spectral measurements and computer processing were the same as those reported previously.^{1,2)}

RESULTS AND DISCUSSION

As described previously,^{1,2)} the background reflectivity decreases rapidly with the metal film thickness. In cases of Cu, Pt, and Ni, infrared measurements were possible up to the film thickness of 3.0 nm, in accord with the case of Au film.²⁾ In the case of Al, on the other hand, there was no decrease in the background reflectivity up to the film thickness of 2.5 nm, and then it decreased with film thickness. Thus, infrared measurements were possible to 4.0 nm thickness.

Intensity enhancement factors of CH stretching bands of 1-monolayer LB films of stearic acid overcoated with Cu, Pt, Ni, and Al films are shown in Figs. 1–4, respectively, as functions of metal film thickness. These factors for p-polarized and s-polarized radiations were identical

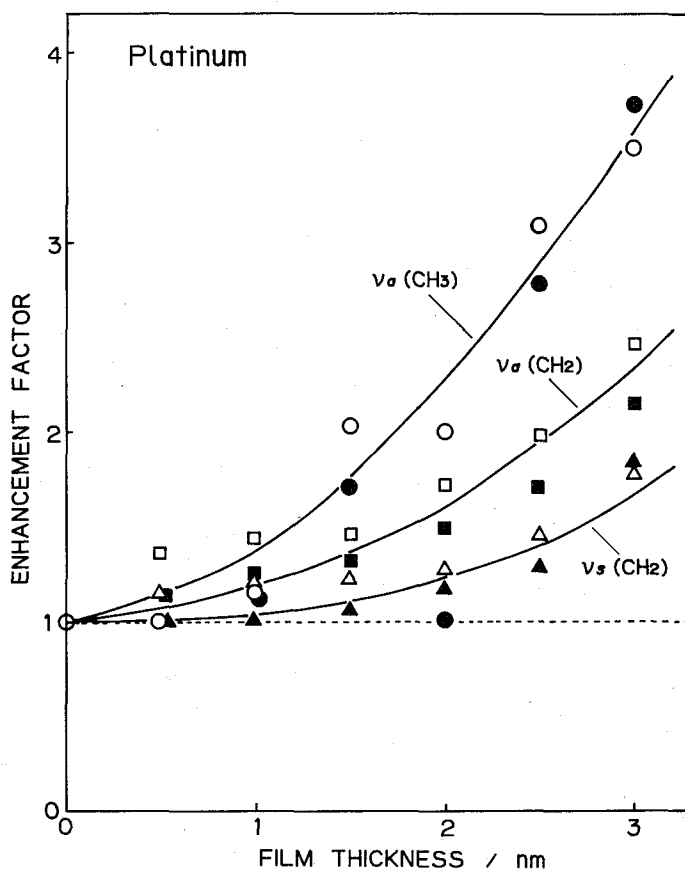


Fig. 2. Intensity enhancement factors for the CH stretching bands of 1-monolayer LB films of stearic acid as functions of Pt film thickness. Open and solid symbols refer to p- and s-polarized radiations, respectively.

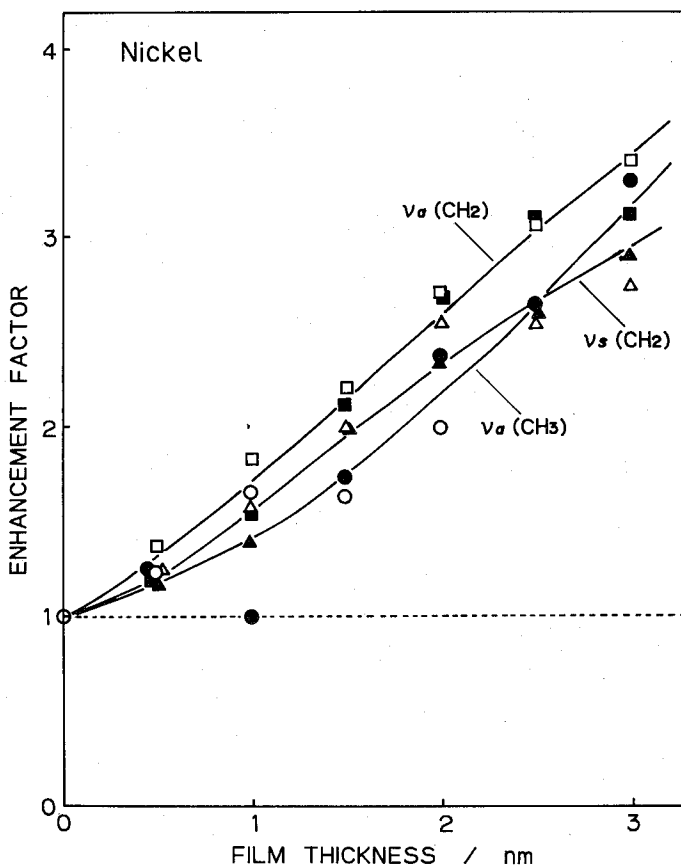


Fig. 3. Intensity enhancement factors for the CH stretching bands of 1-monolayer LB films of stearic acid as functions of Ni film thickness. Open and solid symbols refer to p- and s-polarized radiations, respectively.

within experimental error, suggesting the mechanism of collective electron resonances among small metal islands.^{1,2)} Except for the Al overcoated sample (Fig. 4), the enhancement factors (Figs. 1–3) gradually increase with metal film thickness. In the case of Al overcoated sample (Fig. 4), the enhancement factor starts to increase at *ca.* 2.5 nm thickness, where the background reflectivity starts to decrease as mentioned above.

In all these samples (Figs. 1–4), the maximum intensity enhancement factors for the asymmetric CH_3 stretching band were three to four, much smaller than the corresponding values (*ca.* fifteen) of Ag or Au evaporated samples.^{1,2)} The order of enhancement factors among three CH stretching bands of the Cu and Pt overcoated samples (Figs. 1 and 2) is the asymmetric CH_3 > antisymmetric CH_2 > symmetric CH_2 stretching bands, being in accordance with the previous Ag and Au cases.^{1,2)} However, in the case of Ni and Al overcoated LB films (Figs. 3 and 4), no distinct difference in enhancement factor was observed among these CH stretching bands. The latter two metals are liable to be oxidized when they are exposed to air after vacuum evaporation. If the thin metal film is oxidized, the orientation of the adsorbed monolayer may be disordered.¹³⁾ Further, the surface selection rule of absorption bands

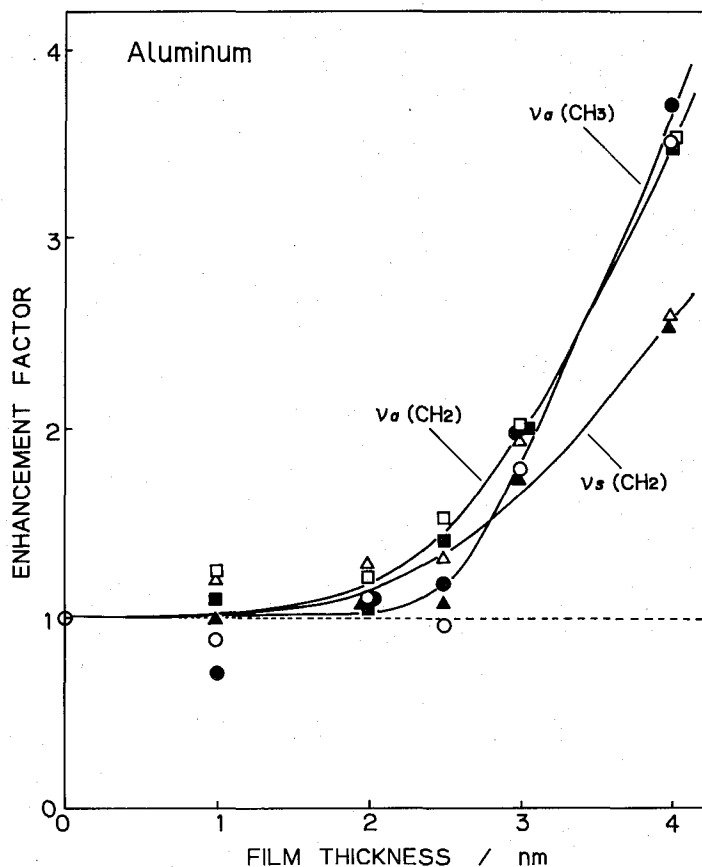


Fig. 4. Intensity enhancement factors for the CH stretching bands of 1-monolayer LB films of stearic acid as functions of Al film thickness. Open and solid symbols refer to p- and s-polarized radiations, respectively.

observed for Ag and Au surfaces^{1,2)} (only the bands with the transition moment component normal to metal surface can be enhanced) may become less effective by the presence of surface metal oxide layers.

In Fig. 5, intensity enhancement factors for the asymmetric CH_3 stretching band of the 1-monolayer LB film of stearic acid are plotted against the metal film thickness for various metals including Ag¹⁾ and Au.²⁾ It can be seen that the intensity enhancement factors in the thickness range 0–3 nm were in the order $\text{Au} > \text{Ag} > \text{Pt} \approx \text{Cu} > \text{Ni} > \text{Al}$. Especially, Au and Ag exhibit large enhancement factors. This result is in conflict with that of the previous paper,¹¹⁾ where Ni is reported to show larger enhancement than Ag.

In the case of SERS, various theoretical approaches have been made to explore the origin of intensity enhancement, and the electromagnetic and chemical effects have been proposed as principal mechanisms.³⁾ The effect due to the increase in the electric field strength on rough metal surfaces has been shown to be roughly proportional to $(\epsilon_1/\epsilon_2)^2$ where ϵ_1 and ϵ_2 is the real and imaginary parts of the complex dielectric constant of the metal ($\epsilon = \epsilon_1 + i\epsilon_2$), respectively.¹⁴⁾ This quantity $(\epsilon_1/\epsilon_2)^2$ may also be used as a convenient guide in the field

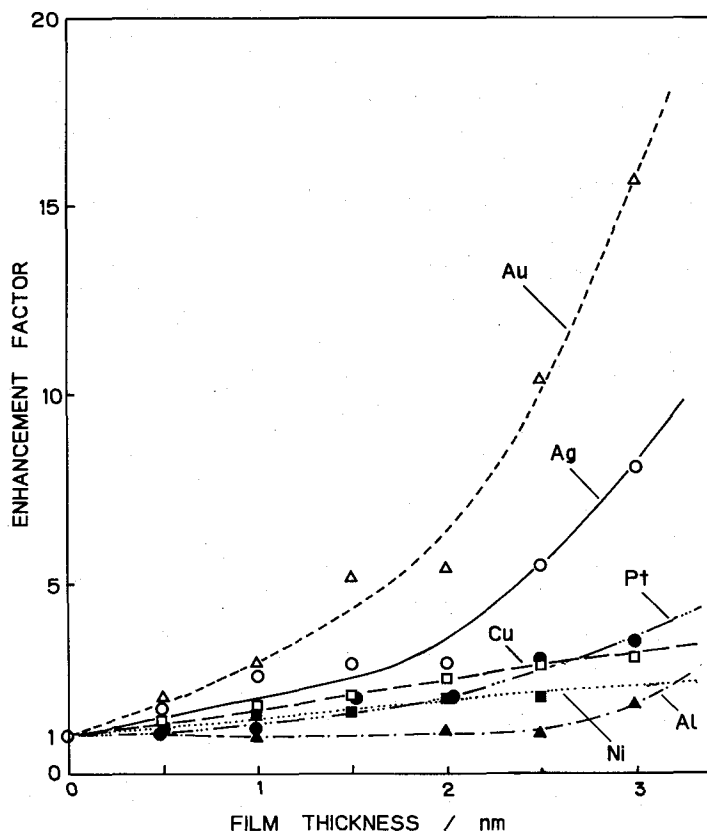


Fig. 5. Metal dependence of intensity enhancement factors of the asymmetric CH_3 stretching band obtained for p-polarized radiation as functions of metal film thickness.

strength enhancements in the infrared region. So, we calculated this quantity for the six metals using reported data of dielectric constants in the infrared region.¹⁵⁾ The results are shown in Fig. 6. In the CH stretching region ($2960\text{--}2850\text{ cm}^{-1}$), the quantities $(\epsilon_1/\epsilon_2)^2$ are in the order $\text{Ag} > \text{Au} > \text{Cu} > \text{Al} > \text{Pt} > \text{Ni}$. This order does not coincide with that in Fig. 5. However, if we consider the liability to oxidation, these discrepancies may be dissolved; the intensity enhancement will be depressed by the formation of surface oxide layer. Reduction of electric field intensity (due to surface plasmon polariton) on metals by the formation of surface oxide layers has been reported by Powell *et al.*¹⁶⁾ Liability to oxidation can be evaluated by the heat of formation of metal oxide. Its order is $\text{Al} > \text{Ni} > \text{Cu} > \text{Ag} > \text{Pt} > \text{Au}$.¹⁷⁾ Therefore, it is reasonable to consider that the enhancement factor of Ag becomes less than that of Au by the oxide formation, and that of Al becomes least.

In summary, the present investigation indicates that the intensity enhancement of infrared ATR spectra of stearic acid LB films by evaporated metal films depends on both dielectric property and liability to oxidation of the metal. This also indicates that the enhancement mechanism is electromagnetic, that is, the collective electron resonances among small metal islands.^{1,2,18)} From the practical point of view, Au and Ag can be used as powerful materials for infrared intensity enhancements, but the other metals cannot.

IR Intensity Enhancement by Evaporated Metals

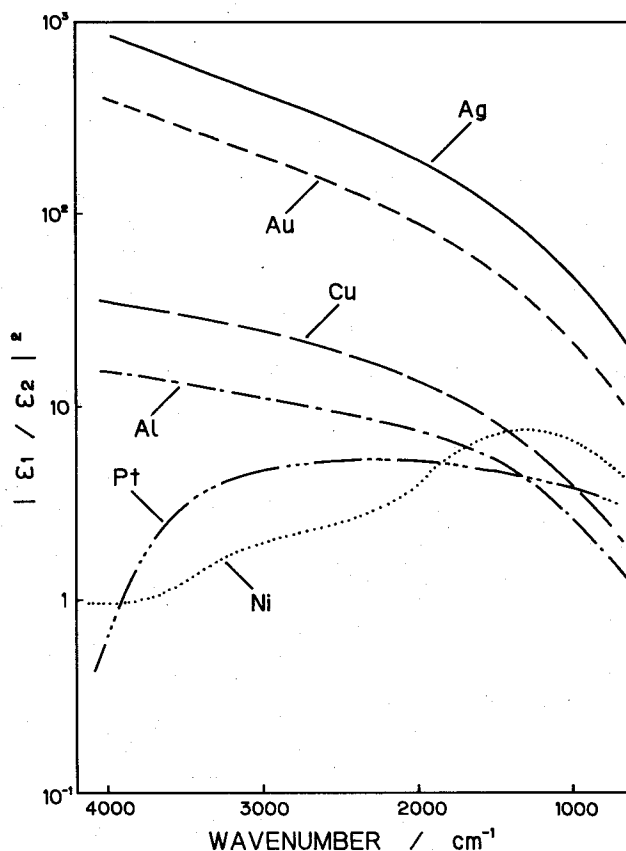


Fig. 6. Metal dependence of $(\epsilon_1/\epsilon_2)^2$ in the infrared region.

REFERENCES

- (1) T. Kamata, A. Kato, J. Umemura, and T. Takenaka, *Langmuir*, to be published.
- (2) T. Kamata, J. Umemura, and T. Takenaka, *Bull. Inst. Chem. Res., Kyoto Univ.*, **65**, 170 (1987).
- (3) R. K. Chang and T. E. Furtak Ed., "Surface Enhanced Raman Scattering," Plenum Press, New York, 1982.
- (4) T. Wood and M. V. Klein, *Solid State Commun.*, **35**, 263 (1980).
- (5) C. S. Allen, G. C. Schatz, and R. P. Van Duyne, *Chem. Phys. Lett.*, **75**, 201 (1980).
- (6) B. H. Loo, *J. Chem. Phys.*, **75**, 5955 (1981).
- (7) H. Yamada and Y. Yamamoto, *Chem. Phys. Lett.*, **77**, 520 (1981).
- (8) T. Lopez-Rios, C. Pettenkofer, I. Pockland, and A. Otto, *Surface Sci.*, **121**, L541 (1982).
- (9) R. Nauman, S. J. Buelow, O. Cheshnovsky, and D. R. Herschbach, *J. Phys. Chem.*, **84**, 2692 (1982).
- (10) T. Takenaka and K. Eda, *J. Colloid Interface Sci.*, **105**, 342 (1985).
- (11) Y. Nakao and H. Yamada, *Surface Sci.*, **176**, 578 (1986).
- (12) F. Kimura, J. Umemura, and T. Takenaka, *Langmuir*, **2**, 96 (1986).
- (13) D. L. Allara and R. G. Nuzzo, *Langmuir*, **1**, 52 (1985).
- (14) J. R. Kirtley, S. S. Jha, and J. C. Tsang, *Solid State Commun.*, **35**, 509 (1980).
- (15) M. A. Ordal, L. L. Long, R. J. Bell, S. E. Bell, R. R. Bell, R. W. Alexander, Jr., and C. A. Ward, *Appl. Optics*, **22**, 1009 (1983).
- (16) C. J. Powell and J. B. Swan, *Phys. Rev.*, **118**, 640 (1960).
- (17) R. C. West, Ed., "Handbook of Chemistry and Physics," 53rd Ed., Chemical Rubber Co., Cleveland, 1972-3.
- (18) M. Moskovits, *J. Chem. Phys.*, **69**, 4159 (1978).