Evaluation of Surface Enhancement Factor $G$

In the IRAS measurement by Cuesta and Cutiérrez of CO adlayer at the polished bulk Ni electrode in the same phosphate buffer solution with pH6.9, the band intensity of CO$_B$ is $8 \times 10^{-4}$ in relative reflectance unit ($\Delta R/R$) with $p$-polarized IR radiation.\(^1\) In our ATR-SEIRAS measurement, the corresponding band intensity reaches $3.4 \times 10^{-2}$ ($\Delta R/R$).

Here, $G$ is simply defined as the ratio of IR band intensities of a molecule adsorbed on a Ni nanofilm and on a smooth bulk Ni surface.\(^2\) $G$ value can be evaluated with necessary calibration of the following factors.

(1) **Calibration of surface coverage**

The surface coverage of CO adlayer at Ni should be larger in previous IRAS than in present ATR-SEIRAS measurement, in considering the fact that CO-saturated phosphate buffer solution was used in the former and the dissolved CO was purged in the latter. Nevertheless, the CO adsorption at a Ni electrode is very strong. In fact, the band intensity increases by only about 10\% if dissolved CO was not removed in the ATR-SEIRAS measurement. Therefore, calibration factor $C_1$ for surface coverage is assumed to be 1.1.

(2) **Calibration of surface roughness factor**

In our ATR-SEIRAS measurement, the surface roughness factor is estimated to be 4.3. In considering that the surface roughness factor for a mechanically polished bulk Ni electrode is about 2.0. Hence, calibration factor $C_2$ for surface roughness is assumed to be 0.47.

(3) **Calibration of incidence angle**
Although the incidence angle $\theta_1$ for the IRAS measurement was not mentioned in Ref 1 in this supporting information, usually, for external IRAS measurement, the incidence angle $\theta_1$ at a flat CaF$_2$ window is 60°. Accordingly, the real incidence angle $\theta_2$ at the Ni electrode in IRAS can be calculated to be ca.42° according to Snell’s law, whereas $\theta_2$ in our ATR-SEIRAS measurement is 70°. Nevertheless, according to the experimental measurement and theoretical calculation by Osawa and his colleagues, when $\theta_2$ is decreased to 42° the band intensity is about 2/3 of that obtained with 70°. Therefore, calibration factor $C_3$ for incidence angle is assumed to be 2/3.

4) Calibration of polarization of IR radiation

In our ATR measurement, unpolarized IR radiation was used. It should be pointed out that theoretically p-polarized radiation will result in at least 2 fold increased band intensity. The argument can be found in Appendix. Therefore, calibration factor $C_4$ for polarization is assumed to be larger than 2.

In summary, we have

$$G = \frac{I_A}{I_E} C_1 C_2 C_3 C_4$$  \hspace{1cm} (1)$$

where $I_A$ and $I_E$ denote the band intensity of CO$_B$ obtained in current ATR-SEIRAS and previous external IRAS measurement, respectively. $C_1$, $C_2$, $C_3$ and $C_4$ are above-mentioned calibration factors, respectively.

$$G > \frac{3.4 \times 10^{-2}}{8 \times 10^{-3}} \times 1.1 \times 0.47 \times \frac{2}{3} \times 2 = 29$$

In practice, $C_4$ can often be as high as 3-4, depending on the morphology and dielectric constant of the metal film. Thus the actual $G$ value may be doubled. It should be also necessary to point out that if integrated band intensities are used for the
evaluation, the actual $G$ value will increase further because of broader band width for CO adlayer at Ni nanofilms.

**Appendix**

In considering this problem, the normalized reflectance change ($\Delta I/I$) is convenient than absorbance.

Unpolarized radiation is decomposed into s- and p-polarized components.

$$I_u = I_p + I_s.$$  

For unpolarized radiation, since s-component does not give absorption,

$$\left(\frac{\Delta I}{I}\right)_u = \frac{\Delta I_p}{I_p + I_s},$$  

while

$$\left(\frac{\Delta I}{I}\right)_p = \frac{\Delta I_p}{I_p}$$

for p-polarization,

If we assume $I_p = I_s$ (that is, $R_p = R_s$), then

$$\left(\frac{\Delta I}{I}\right)_p = 2\left(\frac{\Delta I}{I}\right)_u$$

That is, the peak intensity observed by p-polarization is twice that observed by unpolarized radiation. In the absorbance units, the factor depends on the SEIRA enhancement itself (that is, $(\Delta I/I)_p$).

The actually observed is larger than the simple calculation because $I_p < I_s^{5,6,7}$ which depends on the morphology of the film and the metal (dielectric function).

**References**


