

Potential Dependent Shift of Vibrational Frequencies of Carbon Monoxide Adsorbed on Platinum Group Metals: Stark Effect or Electron Back-Donation?

M. Osawa, M. Sato, and K. Ataka
Catalysis Research Center, Hokkaido University
Sapporo 060-0811, Japan

References

- [1] K. Ataka, Y. Hara, and M. Osawa, *J. Electroanal. Chem.*, **473**, 34 (1999).
[2] Z.Q Fen, T. Sagara, and K. Niki, *Anal. Chem.*, **67**, 3564 (1995).

The stretching vibration of CO adsorbed on Pt and Pt-group metal electrodes shifts with the applied potential. The shift has been explained by Stark effect and/or electron back-donation from the electrode to the $2\pi^*$ anti-bonding orbital of CO. Stark effect assumes that the large potential drop at the interface affects molecular vibrations. If Stark effect is responsible, the rate of the spectral changes should be synchronized with the actual potential changes at the interface, i.e. double-layer charging. On the other hand, if the electron back-donation mechanism is responsible, the rate will be much faster than the double-layer charging. To define which mechanism is more responsible to the potential-dependent peak shift, we have examined the rate of the peak shift for potential modulations by surface-enhanced infrared absorption spectroscopy, in which the phase lag of the infrared response with respect to potential modulations is measured [1].

The experimental details was described elsewhere [1]. A Rh thin film electrode was prepared by electrochemical deposition on top of a 20-nm thick Au film vacuum evaporated on a Si prism. The electrolyte solution used was 0.1 M HClO₄ and CO was adsorbed on the electrode in the double-layer region. The use of a step-scan FR-IR spectrometer enabled us to modulate the potential independent of the interferometer scans. The modulation frequency used in the present study was from 40 Hz to 3 kHz. In-phase and quadrature components of the infrared signal with respect to the potential modulation were measured with a lock-in amplifier.

The intensities of the stretching bands of on-top CO in in-phase and quadrature spectra (Re and Im, respectively) were plotted in Fig. 1. The data points form a semicircle as is observed in ac impedance spectroscopy, suggesting an electron transfer process. By using theoretical equations of Sagara et al. [2], the rate constant of about $5 \times 10^7 \text{ s}^{-1}$ was estimated from the data. This value is very much larger than that of the double-layer charging measured by ac impedance technique ($1 \times 10^3 \text{ s}^{-1}$). Therefore, the electron back-donation mechanism is more likely to contribute to the potential-dependent peak shift than Stark effect.

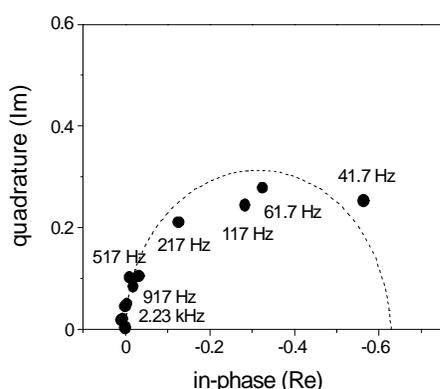


Fig. 1. Cole-Cole plot of the band intensities of on-top CO in in-phase and quadrature spectra.