ADDITIONS AND CORRECTIONS

1998, Vol. 102B

S. Zou, C. T. Williams, E. K.-Y. Chen, and M. J. Weaver*: Surface-Enhanced Raman Scattering as a Ubiquitous Vibrational Probe of Transition-Metal Interfaces: Benzene and Related Chemisorbates on Palladium and Rhodium in Aqueous Solution

Page 9039. The published article includes surface-enhanced Raman (SER) spectra for 20 mM benzonitrile on palladium film electrodes in aqueous 0.1M $HClO_4$ (Figure 2, top; Figure 3, lower). Unfortunately, these spectra were obtained using a band-pass (ca. 25 cm^{-1}) that was insufficient to fully characterize or resolve some vibrational details associated with the aromatic ring. The corrected spectrum shown to the right (Figure 1) was obtained for essentially the same experimental conditions as Figure 2, but with a markedly narrower band-pass (5 cm^{-1}), and 60 s acquisition time.

While the broad-based spectral features are largely unchanged, the improved resolution sharpens the appearance of several bands from aromatic ring modes, especially the ν_{12} trigonal breathing (998 cm^{-1}), the ν_{6a} in-plane bend (492 cm^{-1}), and the ν_{8a} C−C stretch (1590 cm^{-1}), and yields a now-resolved ν_{9a}/ν_{13} pair (1175/1195 cm^{-1}) and a readily discernible ν_{18a} feature (1024 cm^{-1}). The observed small (<5−10 cm^{-1}) peak frequency shifts from the uncoordinated (liquid-phase) Raman spectrum, along with the narrow bandwidths (fwhm ≤ 15 cm^{-1}), provide strong evidence for benzonitrile binding to the transition-metal surface as occurring exclusively via the nitrile group, with the aromatic ring pendent, supporting further the interpretation given in the paper (cf., ref 1). The broader 770 cm^{-1} feature probably arises from overlap between the near-degenerate ν_1 ring breathing and ν_{11} C−H bending modes.

The relative band intensities, as tabulated in Table 2 of the paper, are largely unchanged (within 1.5−2-fold), leaving unaltered the selection-rule arguments based on "relative surface-enhancement factors". The SER spectra for benzene and toluene on palladium and rhodium surfaces described in the paper are entirely unaffected. However, the revised benzonitrile results provide a sharper contrast to the broadened (and frequency-shifted) SER features observed for adsorbed toluene on palladium (Figure 2, lower), demonstrating in more striking fashion the effects of molecular anchoring via the toluene aromatic ring on the surface vibrational spectra.

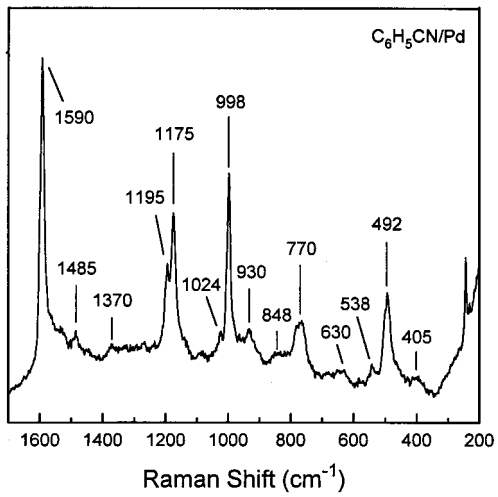

Figure 1.

References and Notes

(1) (a) Gao, X.; Davies, J. P.; Weaver, M. J. *J. Phys. Chem.* **1990**, *94*, 6858. (b) Gao, P.; Weaver, M. J. *J. Phys. Chem.* **1985**, *89*, 5040.

10.1021/jp984245y
Published on Web 11/26/1998