

Effect of Microscopic Surface Roughness in Surface-Enhanced Infrared Absorption Spectrometry

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A surface selection rule has previously been proposed for surface-enhanced infrared absorption that is analogous to the corresponding rule for bulk metals, in that molecular vibrations whose dipole moment change is perpendicular to the surface of the metal will be observable, and those vibrations whose dipole moment change is parallel will be forbidden. In the present study, it was observed that these selection rules may not be applicable under all circumstances, due to the roughness of the metal surface. It was also postulated that there may be more than one type of adsorbate species, either due to different surface sites or due to different adsorption geometry. In some cases, the surface selection rule is obeyed, and in others it appears to be broken.

Introduction

The phenomenon of surface-enhanced infrared absorption (SEIRA) was first observed by Hartstein et al.¹ in 1980 and has been a subject of increased interest in the last five years. The presence in SEIRA spectra of some absorption bands and the absence of others, as compared to transmission spectra, has led to investigations into the possible applicability of surface selection rules similar to those observed in reflection–absorption spectrometry (RAS). Badilescu and co-workers² investigated the surface-enhanced spectrometry of *ortho*-, *meta*-, and *para*-nitrobenzoic acids (*o*-NBA, *m*-NBA, and *p*-NBA, respectively) in an effort to determine the influence of geometrical isomerism on the observed SEIRA spectra. They observed that the intensities of the antisymmetric and symmetric NO₂ stretching bands varied depending on the isomer, but did not draw any general conclusions from this.

Osawa et al.^{3,4} also investigated the SEIRA spectra of *m*-NBA and *p*-NBA. They compared the reflection–absorption spectrum of both nitrobenzoates on bulk silver, the SEIRA spectrum on silver, and the potassium nitrobenzoate salts. From the absence of the $\nu_{\text{as}} \text{CO}_2^-$ stretching band in SEIRA and reflection–absorption spectra (RAS) and the presence of this band in the transmission spectrum of potassium *p*-nitrobenzoate, they concluded that a surface selection rule, similar to that observed in RAS, prevents the observation of this band in the surface-enhanced spectrum. Osawa and co-workers discussed their results in terms of the accepted model of adsorption of nitrobenzoic acid to a metal particle that was originally presented by Hatta et al.,⁵ along with their mechanism for surface enhancement. In this model for adsorption, the islands comprising the metal film are assumed to be ellipsoids of rotation, and the *p*-NBA molecule adsorbs perpendicular to the surface through the oxygen atoms of the carboxylate moiety within the nitrobenzoate anion (see Figure 1).

Osawa and colleagues also proposed a model for the electromagnetic portion of surface enhancement. In this model for SEIRA, the electric field is perpendicular to the surface of the metal islands comprising the metal film at every point (see Figure 2). Consequently, only those vibrations whose dipole

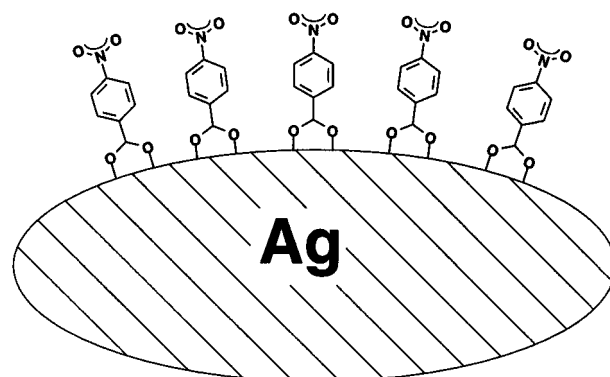


Figure 1. Model for adsorption of *p*-nitrobenzoic acid to a silver particle.

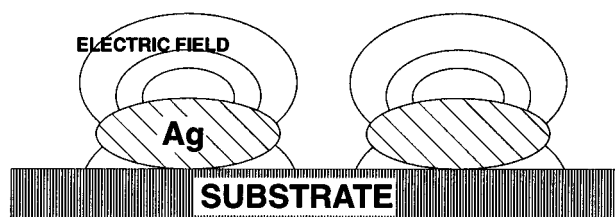


Figure 2. Model for electromagnetic enhancement in SEIRA.

moment change was perpendicular to the surface of the metal film are allowed, and those with dipole moment changes parallel to the surface are forbidden, as the electric field would be perpendicular to the surface, preventing any interaction with a dipole moment change parallel to the surface of the metal.

Preliminary results from our laboratory indicated that these selection rules may not be applicable under all circumstances, and for this reason we undertook to investigate this phenomenon further.

Experimental Section

Thin films of copper or silver (Johnson Matthey, Ward Hill, MA) were deposited on an infrared-transparent substrate, either CaF₂ (McCarthy Scientific, Fullerton, CA) or Ge (Lattice Materials, Bozeman, MT) via physical vapor deposition in a vacuum chamber held at a pressure of 10^{−6} Torr. Thickness of the deposited layer was monitored with a quartz crystal thickness monitor (Kronos, Torrance, CA, Model ADS-200).

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The copper films were 5 nm, and the silver films 10 nm, in thickness. Typical deposition rates were 0.5–0.7 nm/min. 4-Nitrobenzoic acid was acquired from Aldrich (Milwaukee, WI) and used as supplied; 0.001% solutions were made in methanol (Fisher, Pittsburgh, PA). The organic films were generated by depositing an aliquot (typically 20 μ L) of the solution onto the surface of the metal-coated substrate and allowing the solvent to evaporate under cover. The films thus generated were approximately 1 nm thick, given the amount of material used and the area of the substrate. Spectra were obtained with either a Bomem (Quebec City, Canada) MB-100 FTIR spectrometer in transmission or a Perkin-Elmer (Norwalk, CT) 1800 FTIR spectrometer equipped with a Spectra-Tech (Stamford, CT) IR-Plan infrared microscope.

Sodium *p*-nitrobenzoate was prepared by dissolving *p*-nitrobenzoic acid in a dilute solution of sodium hydroxide and allowing the solution to evaporate. Copper *p*-nitrobenzoate was prepared by adding *p*-nitrobenzoic acid (0.36 g) to a solution of 0.13 g of NaOH in 25 mL of H₂O; this solution was then neutralized with 1 M HCl. CuSO₄ (0.28 g) was dissolved and added to the *p*-NBA solution. The resulting precipitate was removed by filtration and recrystallized from water. Spectra of the sodium and copper *p*-nitrobenzoate salts were obtained by diffuse reflection after dilution in diamond dust (to preclude any possibility of ion exchange) with a Spectra-Tech diffuse reflection accessory in a Perkin-Elmer System 2000 FTIR spectrometer.

A multilayer spectrum of *p*-NBA was obtained by depositing an aliquot of a 0.01% solution in methanol onto an infrared-transparent substrate and allowing the solvent to evaporate. A spectrum of an aqueous solution of the *p*-NBA (0.6%) was obtained using an attenuated total reflection (ATR) accessory (Harrick Scientific, Ossining, NY) equipped with a three-reflection zinc selenide ATR element and a solution cell. A transmission spectrum of *p*-NBA as a 0.01% solution in chloroform (Fisher) was obtained in a 0.9 mm cell with KBr windows.

Results and Discussion

Relative Band Intensities. The diffuse reflection spectrum of sodium *p*-nitrobenzoate and the surface-enhanced spectrum of *p*-nitrobenzoic acid on a 10 nm thick silver film are shown in Figure 3. The SEIRA spectrum is consistent with the formation of the carboxylate from the free acid. The relative intensities of the antisymmetric and symmetric NO₂ and CO₂ stretching bands might lead one to suspect that there is some form of selection rule involved in the SEIRA effect; Osawa's published spectra of the potassium salt show similar relative intensities between the bands resulting from the antisymmetric NO₂ and CO₂ vibrations (at 1528 and 1592 cm⁻¹, respectively) and those from the symmetric NO₂ and CO₂ vibrations (at 1352 and 1413 cm⁻¹, respectively), with the bands resulting from the antisymmetric vibrations being significantly stronger than those resulting from the symmetric vibrations.

The diffuse reflection spectrum of the copper *p*-nitrobenzoate salt and the SEIRA spectrum of *p*-nitrobenzoic acid on copper are shown in Figure 4. Note that the relative band intensities are different from those in the spectrum of the sodium salt; the antisymmetric stretching bands are less intense than the symmetric stretching bands, and the relative intensities in the SEIRA spectrum on copper are approximately the same as those in the Cu(*p*-NBA) spectrum. (The derivative-shaped bands in the SEIRA spectrum are reproducible. They are particularly common when copper is the substrate and have been observed by other researchers.⁶)

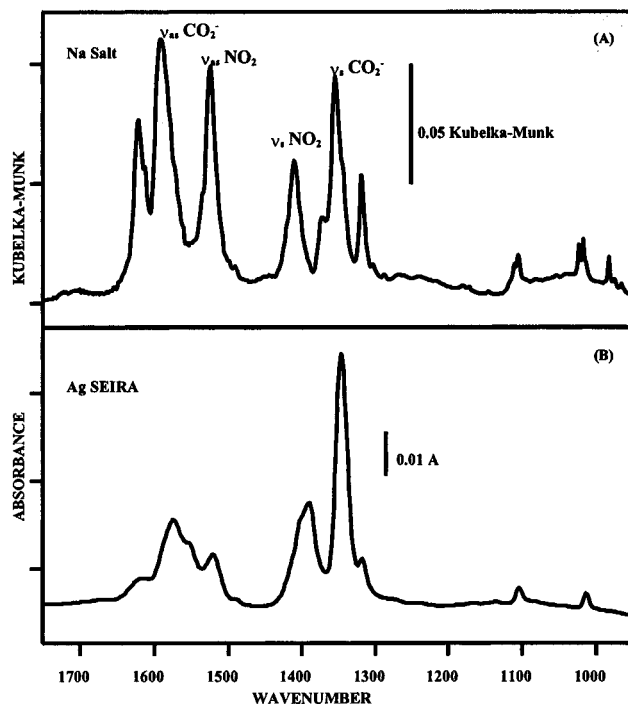


Figure 3. (A) Diffuse reflection spectrum of sodium *p*-nitrobenzoate. (B) Surface-enhanced infrared absorption spectrum of *p*-nitrobenzoic acid on a 10 nm thick silver film.

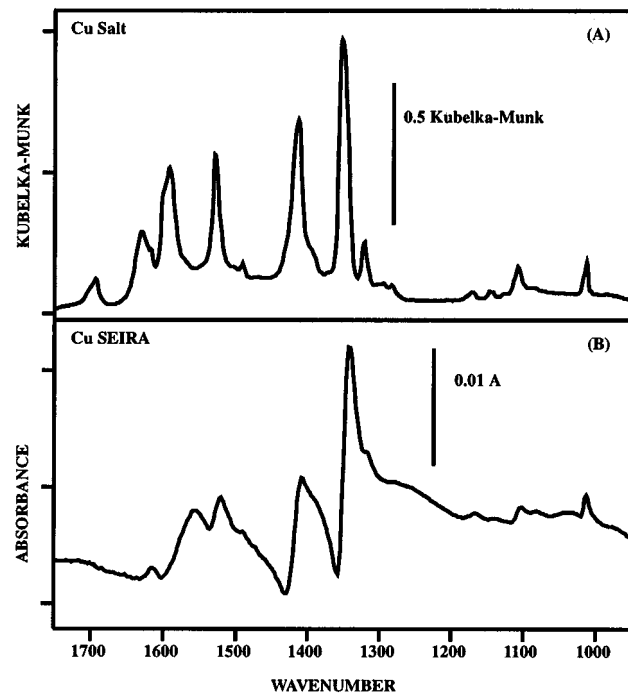


Figure 4. (A) Diffuse reflection spectrum of copper *p*-nitrobenzoate. (B) SEIRA spectrum of *p*-nitrobenzoic acid on a 5 nm copper film.

The difference in relative intensities of the symmetric and antisymmetric NO₂ and CO₂⁻ stretching bands in the spectrum of the sodium salt as compared to those in the copper salt is significant. Nishikawa et al.⁶ published spectra that exhibit bands in the 1600–1500 cm⁻¹ region that correspond to the antisymmetric CO₂⁻ and NO₂ vibrations; yet the presence of these bands was ignored by the authors of this paper, possibly because the weakness of these bands led the authors to assume that they were spurious, an assumption at which one could readily arrive in the absence of spectra of transition-metal salts of the *p*-nitrobenzoate.

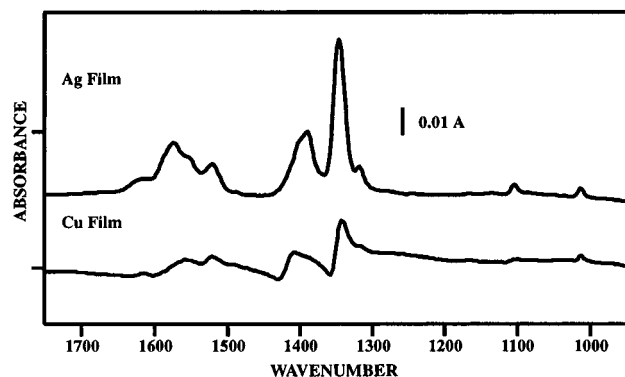


Figure 5. SEIRA spectra of *p*-nitrobenzoic acid on a 5 nm copper film and on a 10 nm silver film.

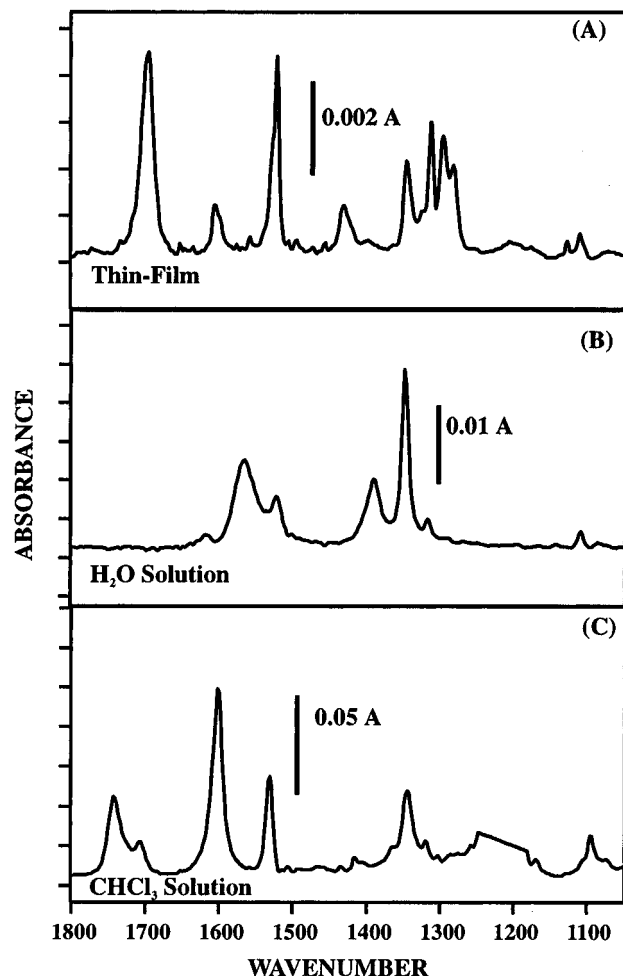


Figure 6. Spectra of *p*-nitrobenzoic acid (A) as a thin cast film, (B) in aqueous solution, and (C) in chloroform solution.

The similarity of SEIRA spectra on copper and silver films is shown by the spectra in Figure 5. The relative intensities and locations of the symmetric and antisymmetric NO₂ stretching bands are similar on both metals; the one notable difference between the SEIRA spectra on these two metals is the higher frequency of the symmetric carboxylate stretch in the case of *p*-NBA on copper ($\Delta\nu = 23 \text{ cm}^{-1}$). This implies that the interactions between the *p*-nitrobenzoate and the surface are similar, whether that surface is copper or silver.

The locations and intensities of the copper and sodium salts of *p*-NBA have been discussed previously; spectra of *p*-NBA as a thin film, in aqueous solution and in chloroform solution are shown in Figure 6. The frequencies of the antisymmetric and symmetric stretching modes of the carboxylate and nitro

TABLE 1: Location (cm^{-1}) of Symmetric and Antisymmetric NO₂ and CO₂⁻ Stretching Bands of *p*-Nitrobenzoic Acid in Different Environments

	band	film	CHCl ₃ sol'n	H ₂ O sol'n	Na salt	Cu salt	Cu SEIRA	Ag SEIRA
ν_s	CO ₂			1389	1410	1413	1407	1384
ν_{as}	CO ₂			1566	1592	1592	1558	1570
ν_s	NO ₂	1346	1343	1347	1354	1352	1342	1343
ν_{as}	NO ₂	1522	1531	1522	1524	1528	1520	1521

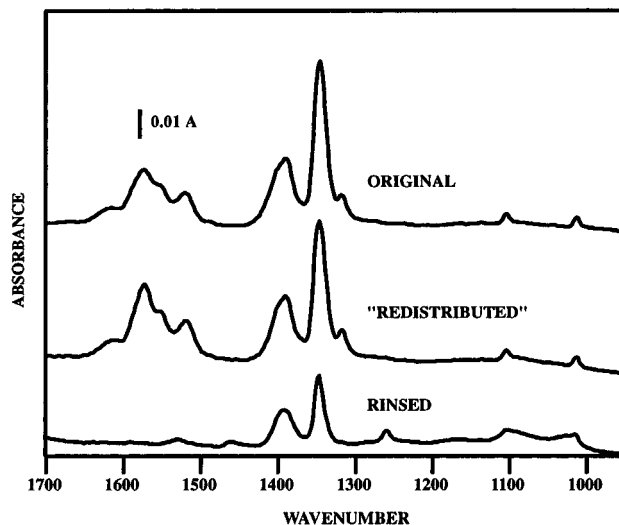


Figure 7. Normal, "redistributed", and "rinsed" deposits of *p*-NBA on a 10 nm silver film.

groups of *p*-NBA measured under different experimental conditions are summarized in Table 1.

These results demonstrate that the location and intensity of the antisymmetric carboxylate stretching band are dependent on the local environment. This variability suggests that one should be cautious in ascribing intensity differences to the action of selection rules.

Multiple Adsorption Sites. The details of sample preparation have varied among different published studies. Osawa et al.⁷ obtained the spectrum of the film cast on the silver island film without further preparation and did not observe the antisymmetric CO₂⁻ or NO₂ stretching bands even though their *p*-NBA film, with a calculated thickness of 1.7 nm, was thicker than those in our experiments. In a later study, Osawa and co-workers³ rinsed the silver surface with acetone after casting the *p*-NBA film in an effort to remove any physisorbed molecules. To investigate the possible consequences of differences in experimental protocol, we first cast a *p*-NBA film on a silver surface and measured the spectrum. Additional methanol was then applied to this film and allowed to evaporate, and the spectrum was measured to determine if the spectrum changed when the *p*-NBA was given the opportunity to migrate to different sites on the silver film. Subsequently, the surface was rinsed with a large volume of methanol and the spectrum measured again. The spectra of the original film, the film after the application and evaporation of methanol, and the rinsed film are shown in Figure 7. There is little difference between the first two spectra, either in the band location or relative absorption intensity of all bands. However, when the surface is rinsed with methanol, two effects are observed: first, the bands corresponding to the antisymmetric NO₂ and CO₂⁻ stretching modes disappear. Second, the intensity of the bands resulting from the NO₂ and CO₂⁻ symmetric stretching modes is reduced by about one-half. This raises the possibility that we are observing two somewhat different chemical species in the initial experiment: one that only gives rise to the symmetric bands and does

not easily rinse off and another in which both sets of bands are visible and is sufficiently labile that it can be removed with a methanol rinse.

Surface Structure and Spectroscopy. *Changes Caused by Adsorption.* The surface selection rules that result from the "standard model" of *p*-NBA adsorption contain two assumptions: that the metal is a smooth, featureless conductor and that the adsorbate is chemisorbed perpendicular to the surface. We believe that in the case of SEIRA spectra neither assumption is necessarily correct.

Effects of Surface Irregularities. An argument that has been made with regard to selection rules has to do with the interaction of the electric field with the surface of the metal islands. From classical electromagnetic theory it can be determined that the lines of flux of the electromagnetic field should be perpendicular to the surface of the metal particles, at least close to the surface, and thus it should be impossible for a dipole moment change parallel to the surface of the metal to interact with the electromagnetic field; thus these modes should not be seen in the infrared spectrum. Greenler et al.⁸ have performed both classical and quantum-mechanical calculations for the interaction of the electromagnetic field with the metal surface for particles of varying sizes and arrived at the conclusion that surface selection rules should apply for particles larger than about 1.5 nm.

The calculations of Greenler et al. assume that the particles are smooth and regular. Our preliminary scanning tunneling microscopy (STM) investigations of the surface⁹ indicate that the silver films are extremely rough on the atomic scale, and thus it seems reasonable that this assumption may not hold. Greenler et al.⁸ determined that the surface selection rule based on electromagnetic field orientation should break down for particles smaller than 0.2–0.6 nm; it does not seem out of the question that the rule could also be expected to break down when the surface of a larger particle contains irregularities on that scale.

If these selection rules are dependent on the smoothness of the surface on an atomic scale, then molecules adsorbed to highly irregular sites on the metal islands could be expected to exhibit infrared spectra that contain the antisymmetric NO₂ and CO₂[−] stretching bands that would otherwise be forbidden for reasons of the electromagnetic field selection rule. Osawa et al.³ suggest that enhancement should be strongest at the tips of the metal ellipsoids comprising the metal film, and it is at these locations of high curvature that the crystal structure can be expected to be the most irregular.

Experimental evidence exists to support our hypothesis with regard to surface irregularities. Ito and co-workers¹⁰ conducted a study in which formic acid was deposited from gas phase onto vapor-deposited copper and nickel films. They noted that in reflection–absorption spectra of this system, both the symmetric and antisymmetric carboxylate bands were visible, but on copper films that were well-annealed, the antisymmetric band was absent. This implies that the copper films that had not been annealed were sufficiently rough on the atomic scale so as to prevent the surface selection rules from applying; after annealing, the metal surface was smooth enough that the assumptions inherent in the surface selection rule model were valid.

Multiple Benzoate Species. Another possibility is that the adsorbed nitrobenzoate exists in several different species, adsorbed to the surface in different ways. Sim and co-workers¹¹ used reflection–absorption infrared spectroscopy to investigate the adsorption of formic acid and formate on single-crystal Ag(111) that had been dosed with oxygen. At low coverages

of formate, they observed only the symmetric CO₂[−] band and concluded that this resulted from bidentate bridging formate whose *C*_{2v} symmetry was preserved by the *C*_{6v} symmetry of the adsorption site. At higher coverages, they observed both the symmetric and antisymmetric carboxylate bands and concluded that these resulted from adsorbed formate species whose molecular plane was tilted from the surface perpendicular, with the result that the antisymmetric carboxylate band would be symmetry-allowed, due to the reduction in symmetry of the adsorbed molecule from *C*_{2v} to *C*_s(2) or *C*₁.

Similar behavior might be expected of the nitrobenzoate anion. At low coverages, adsorption as a bidentate ligand perpendicular to the metal surface at highly symmetric surface sites would explain the absence of the antisymmetric CO₂[−] bands that has been observed by some investigators. At higher coverages, the nitrobenzoate may adsorb as a monodentate ligand, with the other oxygen atom of the carboxylate moiety coordinated to the surface to a greater or lesser extent. This would result in the molecules adsorbing obliquely, causing the antisymmetric CO₂[−] and NO₂ stretching bands to be visible. The steric constraints that cause the nitrobenzoate to adsorb in this fashion may also cause the chemisorption to be weaker, with the molecules thus being more likely to be rinsed off in the experiments described above.

Conclusions

The spectroscopy of any adsorbed species is strongly dependent on its interactions with the adsorbent. We have demonstrated that the standard model that has been used for the adsorption of *p*-nitrobenzoic acid onto silver islands in the context of surface-enhanced infrared absorption spectrometry is oversimplified and thus incomplete. An adequate model for the adsorption must take into account the structural elements that would cause a breakdown in the selection rules based on the orientation of the electromagnetic field that would otherwise apply on a smooth surface. This model would also have to account for the presence of multiple benzoate species adsorbed to the metal surface with different adsorbent/adsorbate geometries. The several adsorbate geometries that result from the adsorption of *p*-NBA onto a silver film that is irregular on the atomic scale cause bands to be observable that in the simple model would be forbidden.

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References and Notes

- (1) Hartstein, A.; Kirtley, J. R.; Tsang, J. C. *Phys. Rev. Lett.* **1980**, *45*, 201–4.
- (2) Badilescu, S.; Ashrit, P. V.; Truong, V.-V.; Badilescu, I. I. *Appl. Spectrosc.* **1989**, *43*, 549–52.
- (3) Osawa, M.; Ataka, K.-I.; Yoshii, K.; Nishikawa, Y. *Appl. Spectrosc.* **1993**, *47*, 1497–1502.
- (4) Osawa, M.; Ataka, K.-I.; Ikeda, M.; Uchihara, H.; Nanba, R. *Anal. Sci.* **1991**, *7* (Suppl), 503.
- (5) Hatta, A.; Suzuki, Y.; Suëtaka, W. *Appl. Phys. A* **1984**, *A35*, 135–40.
- (6) Nishikawa, Y.; Nagasawa, T.; Fujiwara, K.; Osawa, M. *Vib. Spectrosc.* **1993**, *6*, 43–53.
- (7) Osawa, M.; Ikeda, M. *J. Phys. Chem.* **1991**, *95*, 9914–9.
- (8) Greenler, R. G.; Snider, D. R.; Witt, D.; Sorbello, R. S. *Surf. Sci.* **1982**, *118*, 415–28.
- (9) Merklin, G. T.; Bostick, B. C.; Fendorf, S. University of Idaho, unpublished data.
- (10) Ito, M.; Suëtaka, W. *J. Catal.* **1978**, *54*, 13–23.
- (11) Sim, W. S.; Gardner, P.; King, D. A. *J. Phys. Chem.* **1996**, *100*, 12509–16.