Photochemical Desorption of 4-Vinylbenzoic Acid Adsorbed on Silver Colloid Surfaces

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Temporal changes in the surface-enhanced Raman scattering (SERS) of 4-vinylbenzoic acid (4vba) adsorbed on silver colloid surfaces were studied using a method in which the solution of the adsorbate-covered colloid solution flowed through a capillary at differing rates. In this way the photochemical effect of the illuminating laser was studied quantitatively. 4vba appears to exist on the colloid surface in two forms: one that photodesorbs under the influence of the laser and one that does not. An analysis of the SERS spectra suggests that the former adopts a surface geometry in which the benzene ring and carboxylate group are adsorbed flat on surface but where the vinyl group is not bonded directly to the surface. In the latter, all three groups are adsorbed on surface simultaneously: the benzene and vinyl groups are π-bonded, while the carboxylate group is adsorbed through a nonbonding electron pair of one of its oxygens. The photodesorption rate constant was found to be proportional to laser power. Its value was found to be large in the visible region of the spectrum, increasing toward the blue; hence, the photodesorption mechanism is likely initiated by a metal to adsorbate charge-transfer absorption.

Introduction

Enhanced surface photochemistry of molecules adsorbed on surfaces capable of producing surface-enhanced Raman scattering was proposed theoretically and observed experimentally.[1−5] Surface-enhanced Raman scattering (SERS) spectroscopy[6] is a powerful technique for studying surface chemical reactions on the surfaces of colloidal metal aggregates. The change in the concentration of reagents and products can be followed by observing the changes in the SERS spectra of the adsorbed molecules. To date, only a few surface-enhanced photochemical reactions have been reported which were studied by observing the decrease in the photoreagent signal or the increase in the photoproduct signal with time for a sample contained in an ordinary cell. For example, the kinetics of the photodecomposition of 2-pyrazinecarboxylic acid adsorbed on the surface of colloidal silver was studied in this manner.[7] This was possible because that reaction was slow, thereby allowing the changes in the SERS signal to be recorded quantitatively despite the fact that it takes approximately 0.1 s to record a SERS spectrum with an adequate signal/noise ratio. Most surface photoreactions are too rapid to study in this way, and indeed, a number of reported SERS spectra are in fact spectra of the photoproduct(s) of a rapid photochemical reaction which was essentially complete before the spectrum was collected. (Of course, one could follow the time evolution of a single SERS band with a time resolution much shorter than 0.1 s; however, it is preferable and, at times, essential to record complete spectra for a proper analysis of the kinetics.)

Recently, we adapted a flow technique that allows fast photochemical reactions to be studied using SERS. By so doing, the two time scales—that characterizing the SERS measurement and that defining the photochemical rate—can be decoupled, the latter being determined by the mean residence time of the photoreagent, or more precisely the colloid carrying the photoreagent, in the laser beam producing the photochemistry. We have already used this method to study the photoreaction of phthalazine,[8] the photodesorption of *o*-diiodobenzene,[9] and the photoisomerization of maleic acid[10] adsorbed on the silver colloid surface. Here, we report the photodesorption of 4-vinylbenzoic acid adsorbed on the silver colloid surface using the flow method described in refs 8 and 9.

Experimental Section

Silver sols were prepared as described previously.[11] Briefly, 60 mL of a 2×10^{-3} M sodium borohydride solution was mixed with 22 ± 2 mL of a 1×10^{-3} M silver nitrate solution. 4-Vinylbenzoic acid was introduced into the colloid as a methanol solution. One-half milliliter of 2×10^{-1} M 4-vinylbenzoic acid (4vba) in MeOH was added dropwise to 100 mL of silver colloid. Upon adding the adsorbate, the solution turned purple, indicating colloid aggregation. No SERS or Raman bands due to methanol were observed in the SERS spectrum. Poly(vinylpyrrolidone) (PVP, MW 40 000) was added to the solution as a stabilizer, preventing excessive aggregation and eventual flocculation of the colloid. The final concentration of PVP in the solution was approximately 0.014 wt %. Experiments were also carried out in the absence of PVP in order to ascertain that the polymer did not noticeably affect the spectroscopy or the kinetics.

The previously described[8] flow cell consists of a reservoir made from a graduated cylinder whose bottom was cut off and a stopcock attached. A standard 1.8 mm Pyrex capillary, attached with a plastic tube to the reservoir, was used as the Raman cell. The colloid/adsorbate solution was allowed to flow from the reservoir, through the capillary, and into a large basin filled with water to the level of an overflow spout, in order to maintain the final level constant. To minimize turbulence, the outlet tube emptied the colloid under the surface of the water

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in the basin. Colloid samples were used only once in order to avoid contamination by the photoproduct.

Surface-enhanced Raman spectra were excited by a focused beam of an Ar ion (Lexel Model 3000) or a Kr ion laser (Lexel Model 3500) traversing the glass capillary of the flow system. Spectra were recorded using a Spex 1887C Triplemate spectrometer equipped with a multichannel charge-coupled device (CCD) detector and interfaced to an IBM personal computer. Kinetic runs were carried out as a function of laser power (20–50 mW) at 514.5 nm and as a function of laser wavelength for six visible (457.9, 476.5, 496.5, 514.5, 430.9, 568.2 nm) laser lines with 20 mW laser power at the sample. Some spectra were recorded using a Spex 1403 double monochromator equipped with dc detection and excited with a Lexel Model 95 Ar ion laser. The Raman spectrum of solid 4vba was excited with the 1064 nm output of a Nd:YAG laser (Spectra-Physics) and recorded using a Fourier transform Raman spectrometer (Bomen Grams). Raman intensities were calibrated using the Raman spectrum of CCl_4 excited with the same wavelength and power as those used in each subsequent SERS kinetic run. Only relative intensities were required. In order to check the extent of colloid aggregation, UV–vis spectra were recorded using a Varian Cary 3 UV–vis spectrophotometer.

Flow Kinetics

The principle behind the flow cell was discussed in detail in ref 8. Use is made of the fact that the flow rate through a capillary fed from a continuously emptying reservoir decreases with time.[12] An adsorbed photoreagent molecule, swept by the flow through the illuminated spot in the capillary, is exposed for a duration, τ, whose value increases with time as:

$$\tau = \tau_0 \ln\{[A_cL/(A_{gc}h_0)]\exp(t/\tau_0) + 1\} \qquad (1)$$

(the quantities τ_0, A_c, L, A_{gc}, h_0 are respectively $A_{gc}/(\rho g)$, the cross-sectional area of the capillary, the height of the illuminated spot, the cross-sectional area of the reagent reservoir, and its initial height. ρ is the density of the reagent and g is the gravitational acceleration.) The quantity τ initially increases exponentially with time and then switches to a linear increase at very long time. For ideal Poiseuille flow, τ would increase with time strictly exponentially; the revised expression given by eq 1 corrects for the fact that at very slow flows the flow rate as a molecule enters the illuminated spot differs from that when the molecule leaves it.[13]

The laser beam serves a dual purpose: promoting the photoreaction and exciting the SERS signal. The SERS spectrum will reflect the average reagent and product concentrations present in the illuminated portion of the capillary. Using the same simplifications that were made in the analysis described in ref 8, the average reagent concentration, $\bar{A}$, in the illuminated spot is given by

$$\bar{A} = \{A_0/(k_1\tau)\}[1 - \exp(-k_1\tau)] \qquad (2)$$

where A_0 is the initial concentration of A. In obtaining eq 2, we assumed that the photoreaction is pseudo-first-order in A, as would be the case for a unimolecular photodecomposition or for photodesorption. The rate constant k_1 will, in general, depend on the laser intensity, I, as $k_1 = aI^n$, where n is the apparent number of laser photons required to initiate the photoreaction and a is a wavelength-dependent quantity proportional to the absorption cross section.

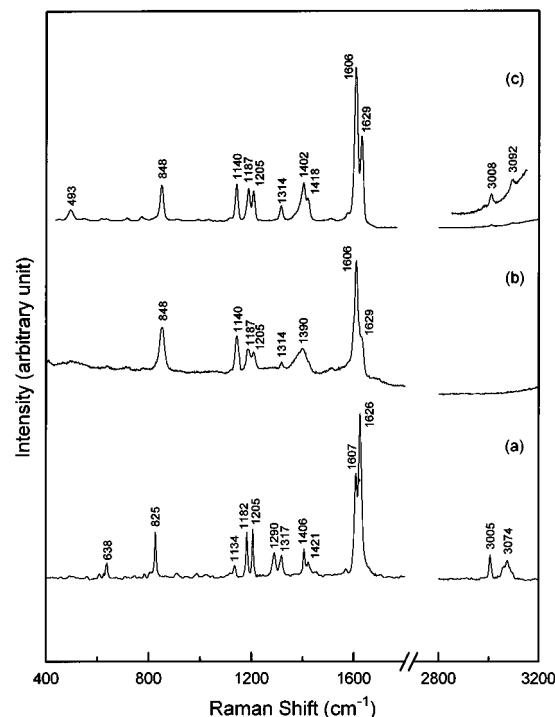The Raman intensity associated with a reagent band will have the form

Figure 1. (a) FT-Raman spectrum of solid 4-vinylbenzoic acid, (b) SERS spectrum of 4-vinylbenzoic acid adsorbed on silver colloid recorded using a scanning spectrometer, and (c) SERS spectrum of 4-vinylbenzoic acid recorded under fast flow conditions using a multichannel spectrometer (514.5 nm Ar^+ laser excitation and 20 mW).

$$I_{Raman} = I\sigma_A\bar{A} + b_A \qquad (3)$$

where σ_A is proportional to the (band-specific) Raman cross section, I is the laser intensity and b_A is a baseline function.

Results and Discussion

The FT Raman spectrum of solid 4-vinylbenzoic acid (4vba) and the SERS spectra of 4vba adsorbed on colloidal silver recorded with scanning single-channel and multichannel spectrometers are shown in Figure 1. The SERS spectrum shown in Figure 1b was obtained using a scanning single-channel spectrometer from a sample contained in a capillary, without flow. The spectrum shown in Figure 1c, which is the same as the lowest spectrum of Figure 2, was recorded under fast flow conditions using a multichannel spectrometer. The two spectra differ with respect to the relative intensities of several bands and the presence or absence of others, suggesting that the spectrum observed for the nonflowing sample reflects the effect of a photoprocess.

Assignments of the vibrational modes of 4vba were made by comparing the frequencies of the observed bands with those of known modes of benzoic acid and styrene, which have a similar structures, using the vibrational data of Varsanyi[14] and Dollish et al.[15] In the solid spectrum, the bands related to modes of the benzene ring are at 607, 825, 987, 1134, 1182, 1205, 1570, 1607, and 3074 cm^{-1}. These are assigned to ν_{6b}, ν_{10a}, ν_{12}, ν_{18b}, ν_{9a}, ν_{13}, ν_{8b}, ν_{8a}, and ν_2, respectively. The bands at 638, 1290, and 1406 cm^{-1} are ascribed to $\gamma(C{=}O)$, $\nu(C{-}OH)$, and $\beta(OH)$, respectively, while the bands at 908, 1317, 1626, and 3005 cm^{-1} are assigned to $\gamma_s({=}CH_2)$, $\beta({=}CH)$, $\beta_s({=}CH_2)$, $\nu(C{=}C)$, and $\nu({=}CH)$, respectively. The peak positions and their vibrational assignments are summarized in Table 1.

Spectra b and c of Figure 1 differ in a number of respects. Some bands which are distinct in spectrum c are very weak or absent in spectrum b. For example, the band at 1606 cm^{-1} (ν_{8a})

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TABLE 1: Spectral Data and Vibrational Assignments for 4-Vinylbenzoic Acid

benzoic acid solid[a]	styrene liquid[a]	4-vinylbenzoic acid			assign[e]
		SERS			
		solid[b]	sol[c]	sol[d]	
420					β(C–(OH))
	443				6a
				493	γ_S(C=CH$_2$)
	555	558			16b
617	620	607			6b
		638			γ(C=O)
710		710			β(C=O)
794	775	783	772		11
853	839	825			10a
			848	848	δ(COO$^-$)
	909	908			γ_S(=CH$_2$)
1001	999	987			12
1027	1033				18a
1132		1134	1140	1140	18b
1157	1156				9b
1179	1181	1182	1187	1187	9a
	1203	1205	1205	1205	13
1289		1290			ν(C–(OH))
1323	1316	1317	1314	1314	β(=CH$^-$)
			1390	1402	ν_s(COO$^-$)
		1406			β(OH)
	1412	1421		1418	β_S(=CH$_2$)
1444	1447	1450			19b
	1494				19a
	1575	1570	1572		8b
1603	1601	1607	1606	1606	8a
	1630	1626	1629	1629	ν(C=C)
1633					ν(C=O)
2592		2587			ν(OH)
3009	3009	3005		3008	ν(=CH$^-$)
3073	3061	3074			2
	3089			3092	ν_{as}(=CH$_2$)

[a] Ordinary Raman. [b] FT-Raman. [c] Single channel without flow. [d] Multichannel with flow. [e] Denoted in term of Wilson's notation.

is strong in both spectra while the band at 1629 cm^{-1}, which is assigned to a $\nu_{C=C}$ mode, is relatively weak in spectrum b. The bands at 849 and 1390 cm^{-1} are assigned to δ(COO$^-$) and ν_s(COO$^-$), respectively. No band assignable to a C=O stretching vibration ($\nu_{C=O}$) is present in any of the SERS spectra while the symmetric stretching and deformation bands of the carboxylate group are distinctly visible at approximately 1400 and 849 cm^{-1}, respectively. This implies that the carboxylic acid group is adsorbed on the surface as the carboxylate, and the SERS band at 1402 cm^{-1}, which is close in frequency to the β_{OH} mode at 1406 cm^{-1}, in the spectrum of the solid, is assigned exclusively to $\nu_{s,COO}^-$, which also appears in that vicinity. Additional evidence for this assignment is provided by the fact that ν_{OH}, which is expected near 2600 cm^{-1}, is absent from the SERS spectrum but present in the Raman spectrum of the solid (see Table 1). The bands at 494, 1315, 1418, 3008, and 3092 cm^{-1} are assigned to γ_s(=CH$_2$), β(=CH$^-$), β_s(=CH$_2$), ν(C=C), ν(=CH), and ν_{as}(=CH$^-$), respectively.

A representative series of SERS spectra of 4vba adsorbed on silver colloid, recorded under flow condition and excited with 514.5 nm Ar ion laser light are shown in Figures 2 and 3. The traces correspond (bottom to top) to the 2nd, 50th, 100th, 150th, and 200th scan of a series of 200 spectra collected in sequence and with equal time between each. The entire series took 1000 s to record; hence the time between scans was 5 s. Measurements were also made with 457.9, 476.5, 496.5, 530.9, and 568.2 nm excitation using Ar or Kr ion lasers. Except for the actual rates, the overall spectroscopic trends were very similar for all excitations, and only a series of spectra excited with 514.5 nm are shown.
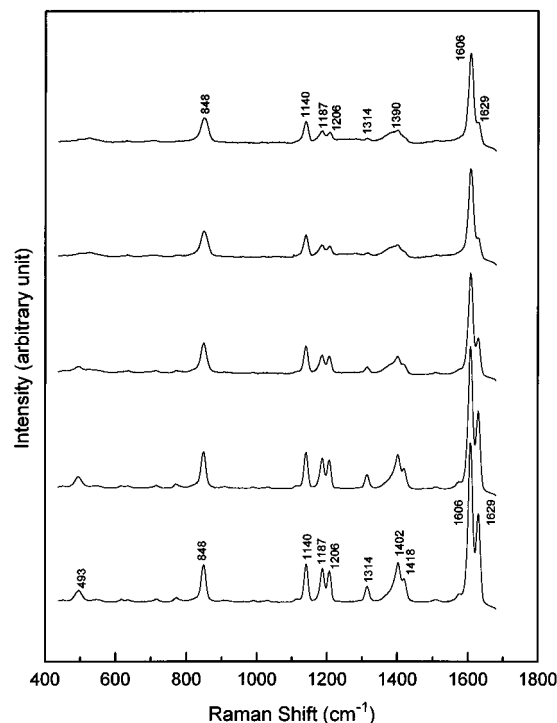

Figure 2. The 2nd, 50th, 100th, 150th, and 200th SERS spectra (bottom to top) of 4-vinylbenzoic acid adsorbed on silver colloid of a series of spectra recorded using multichannel detection and conditions of progressively decreasing flow rate (514.5 nm Ar$^+$ laser excitation and 20 mW).
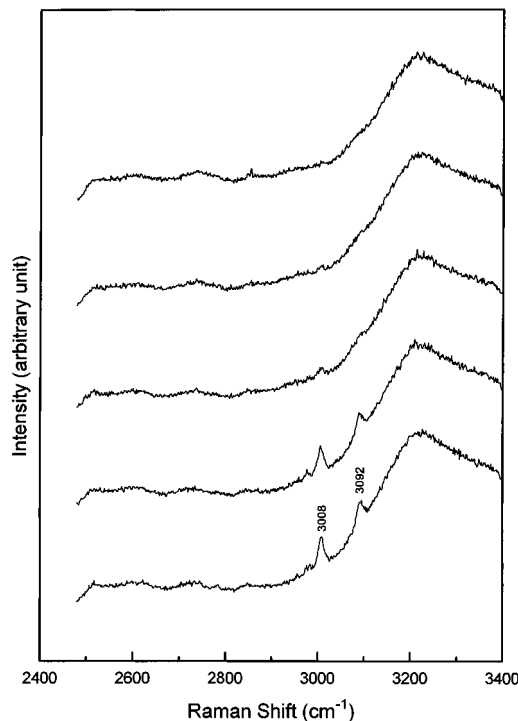

Figure 3. As in Figure 2, but showing the CH stretching frequency range.

The effects of exposure of the sample consisting of 4vba adsorbed on silver colloid to the laser light on the observed SERS spectra fall into three categories. Several bands decrease in intensity to a certain level and then decrease no further, e.g., the bands at 1140 and 1606 cm^{-1}. Others, such as the band at 849 cm^{-1}, do not appear to decrease in intensity at all with laser irradiation. Still others, such as those at 1315, 1402, 1629, 3008, and 3092 cm^{-1}, corresponding to β(=CH$_2$), ν_s(COO$^-$),

$\nu(C=C)$, $\nu(=CH)$, and $\nu_{as}(=CH-)$, respectively, decrease almost to zero intensity, and when they do, there is no further change in the intensity of the remaining bands. All of the above-mentioned bands except for the band at 1402 cm^{-1}, which is due to $\nu_s(COO^-)$, are vibrational modes of the vinyl group. Following the rapid decrease of the band at 1402 cm^{-1}, only a weak broad band centered at 1390 cm^{-1} remains behind in that region of the spectrum. This broad band likely belongs to $\nu_s(COO^-)$. The band at 849 cm^{-1} is assigned to a COO$^-$ deformation mode. Although its overall intensity decreases only slightly with laser irradiation, its bandwidth increases with increasing exposure time. All of the bands that decrease in intensity with laser irradiation do so at the same rate.

The above observations imply that there are two species initially adsorbed on the silver colloid surface, one of which remains on the surface despite laser irradiation while the other is photoactive. Many of the SERS bands of the two species are coincident in frequency, as a result, some bands are observed to decrease in intensity up to a point and then stop. A few are unique to the two species. Moreover, all of the observed bands can be easily assigned to adsorbed 4vba. Hence, we propose that both species are 4-vinylbenzoic acid adsorbed on the surface at different sites or with different surface orientation or both. And the few unique bands observed for the two individual species result from the action of surface selection rules, making some bands intense while others are weak due primarily to the orientation of the molecule with respect to the local surface. The surface coverage of one of these species decreases substantially with laser illumination. We ascribe this disappearance to photodesorption rather than to photodecomposition, or some other photochemical process, since we observe no photoproduct growing in as the photoreagent concentration diminishes. Of course, we cannot exclude the possibility that the adsorbed molecule actually photoreacts to form an intermediate species that then desorbs from the surface. The other form of 4vba remains on the surface.

A clue as to the nature of the surface geometry of the two adsorbate species is first provided by the CH stretching region of their SERS spectra. Only CH stretching bands belonging to vibrations of the vinyl group are ever observed. These decrease with increasing irradiation, ultimately disappearing. Specifically, no CH vibrations due to the benzene ring are observed either initially or after exposure to the laser. This implies that the benzene ring in both forms of the adsorbed 4vba is almost parallel to the surface.[16a] By contrast, the vinyl group of the species that is photodesorbed must be oriented such that it is inclined so as to have a nonnegligible normal component with respect to the local surface. On the other hand, the surface geometry of the species that is not photodesorbed must be such that both its benzene ring and vinyl groups are parallel to the surface.

Next we consider the disposition of the carboxylate groups in the two species. The two strong SERS bands associated with vibrations of the carboxylate group are the $\nu_s(COO^-)$ band at approximately 1390 cm^{-1} and $\delta(COO^-)$ at approximately 850 cm^{-1}. The relative intensities of these two bands depend on the surface geometry of the COO$^-$ group. Three major classes of bonding geometry can be envisioned for the carboxylate group on the silver surface: (i) a flat geometry where the carbon atom and two oxygens occupy a plane more or less parallel to the surface, (ii) a chelating or standing up geometry, in which both oxygens are more or less equally bonded to the surface but the carbon atom lies significantly off the surface, and (iii) a one-legged geometry in which most of the surface bonding is through a single oxygen atom and the plane of the COO$^-$ group
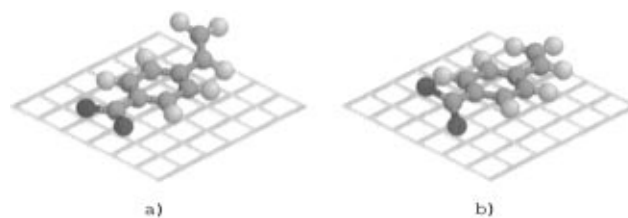

Figure 4. Suggested surface geometries of the two species of 4-vinylbenzoic acid adsorbed on silver colloid surface. (a) The form that photodesorbs. Bonding is mainly through the phenyl ring and weakly bonded (flat) carboxylate group. The vinyl group is tilted away from the surface. (b) The form that does not photodesorb forms π bonds through both the phenyl and vinyl groups and a σ bond through one of the carboxylate oxygens.

is perpendicular to the surface. Suh and Kim[16b] analyzed the SERS spectra of seven aromatic carboxylates of known surface geometry and concluded that, for molecules whose carboxylate groups were bound to the surface in the flat geometry, ν_s(COO$^-$) is very strong while δ(COO$^-$) is very weak. For molecules bound "standing up" both bands are strong, but the ν_s(COO$^-$) band is more intense than the δ(COO$^-$) band. For molecules adopting the one-legged geometry the δ(COO$^-$) band is stronger than the ν_s(COO$^-$) band.

After prolonged laser irradiation (see, for example, the top spectrum in Figure 2), the intensity of ν_s(COO$^-$) is somewhat stronger than that of δ(COO$^-$), suggesting that the carboxylate group of the species remaining on the surface after irradiation is bound in the one-legged fashion. In contrast, the ν_s(COO$^-$) band at 1402 cm^{-1} decreases in intensity and ultimately disappears while the intensity of the δ(COO$^-$) band at 848 cm^{-1} is almost unchanged with laser exposure. Hence, the COO$^-$ group of the species, which is photodesorbed, appears to rest flat on the silver surface since ν_s (COO$^-$) is intense while δ(COO$^-$) is very weak. On the basis of these arguments the two forms of 4vba initially adsorbed on the silver colloid are proposed to be disposed as shown in Figure 4: (a) being the form which is photodesorbed while (b) is the species that appears to remain on the surface after irradiation. In both forms the benzene ring is parallel to the surface.

The geometry of the species which does not photodesorb (Figure 4b) is such that all three groups—the carboxylate group, the benzene ring, and the vinyl group—can bind to the surface simultaneously: the benzene ring and vinyl group through their π electrons and the carboxylate group through the σ electrons of one of its oxygens. The resulting very strong bond is likely the reason for its reluctance to photodesorb. Contrariwise, the species that photodesorbs binds almost exclusively through the π electrons of the benzene ring since the vinyl group is inclined to the plane of the surface and, therefore, not able to π-bond effectively, and the flat geometry of the carboxylate is an unfavorable one for strong binding to the metal. The latter point is also in keeping with the observed frequencies associated with the carboxylate group in the two species. In the more strongly bound form of 4vba, ν_s(COO$^-$) appears near 1390 cm^{-1}, signifying a rather strong bond between the carboxylate group and the surface in that species, while for the photodesorbed species it appears at the relatively high value of 1402 cm^{-1}. An analysis using molecular models of the 4vba molecule and a silver surface shows that the length scale is such that the strongly bound form of 4vba (Figure 4b) can be placed on a Ag(111) surface in a particularly favorable fashion for bonding. If the phenyl ring is placed over a 3-fold surface site, then the carboxylate group falls on top of another silver atom while the vinyl ring can bind to yet another surface Ag atom. (Five Ag atoms are involved in all.) Covering the surface with as many
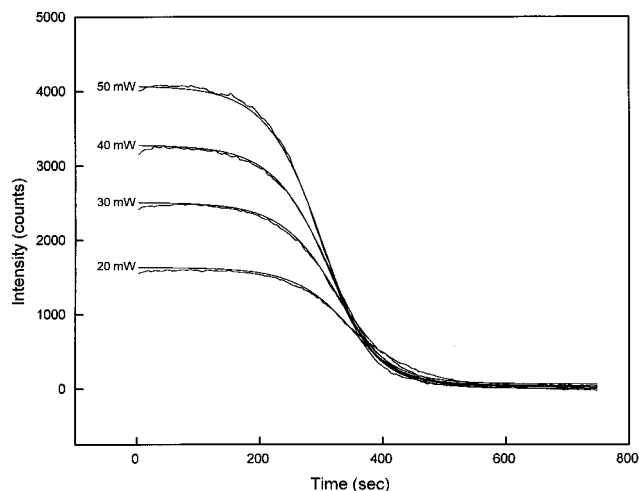
Figure 5. Time evolution of the SERS intensity of the 1606 cm^{-1} band of 4vba excited with 514.5 nm Ar$^+$ laser radiation. Jagged lines are (base line subtracted) experimental data; smooth lines are recalculated according to the model described in the text. The laser power from top to bottom: 50, 40, 30, and 20 mW.

Figure 6. Time evolution of the SERS intensity of the 1606 cm^{-1} band of 4vba excited with several Ar$^+$ and Kr$^+$ laser lines. The laser power was 20 mW in every case. Jagged lines are (base line subtracted) experimental data; smooth lines are recalculated according to the model described in the text.

4vba molecules disposed in this manner still leaves surface binding sites that can accommodate adsorbate requiring a smaller area. Hence, the weakly bound form of 4vba (Figure 4a), i.e., the form that photodesorbs, might incline its vinyl group away from the surface in order to fit into one of these smaller adsorption sites. Of course, the surface of the colloid is not exclusively (111), although there probably exists a great deal of Ag(111) since silver prefers to show this face. In fact, this entire explanation for the observation of two forms of adsorbed 4vba, although plausible, is speculative and is introduced heuristically. It is also possible, for example, that one form of 4vba photodesorbs while the other does not, because the local band structure of one allows a resonance at our photon energies while the other does not. This is a less likely explanation, however, in view of the expected richness of the band structure of a species chemisorbing on silver in this energy range. Nevertheless, other explanations are possible, and our data do not point to any explanation unequivocally.

The time evolution of the SERS intensity of the band at 1606 cm^{-1} during irradiation with a 514.5 nm Ar ion laser light is shown in Figure 5 for a series of laser powers ranging from 20 to 50 mW. The four traces represent differing laser intensity. The jagged lines are experimental data, and the smooth lines are recalculated curves obtained by fitting the experimental data to eqs 1–3. The best fit was obtained with $a = 1.92$ s^{-1} mW^{-1} and $n = 0.98$, where these constants refer to the rate constant written in the form $k_1 = aI^n$. The four curves in Figure 5 were fit simultaneously using a single set of parameter values but independent values for the base lines. A value of $\tau_0 = 52.5$ s was returned by the fit. Acceptable fits were obtained with n in the range 0.96–0.98. The experimental data could not be fit with n equal to or in the vicinity of 2. We conclude that 4vba undergoes a photochemical process on the silver colloid surface which is initiated by the absorption of one photon.

The photochemical rate constant was found to be wavelength dependent in the visible region. The time evolution of the SERS band intensity at 1606 cm^{-1} is shown in Figure 6 for six excitation wavelengths. The rate of photodesorption increases rapidly on going toward the blue. With 20 mW laser power, the values of the rate constant, k_1, obtained by fitting eqs 1–3 to the data shown in Figure 6 are found to be 15.9, 24.7, 38.4, 43.1, 52.0, and 65.2 s^{-1} for 568.2, 530.9, 514.5, 496.5, 476.5, and 457.9 nm Ar or Kr ion laser irradiation, respectively. The rate constants are plotted in Figure 7 as a function of excitation
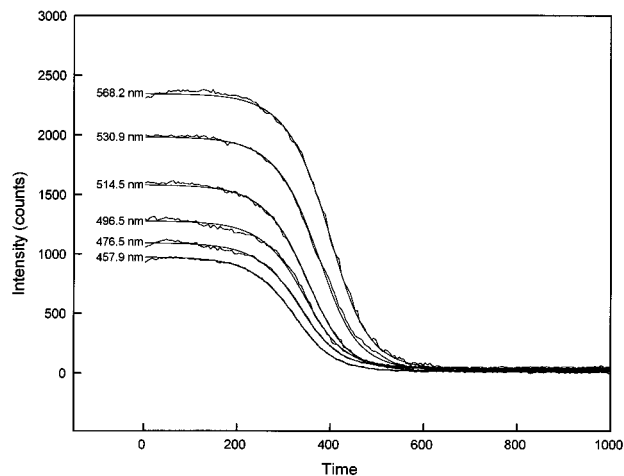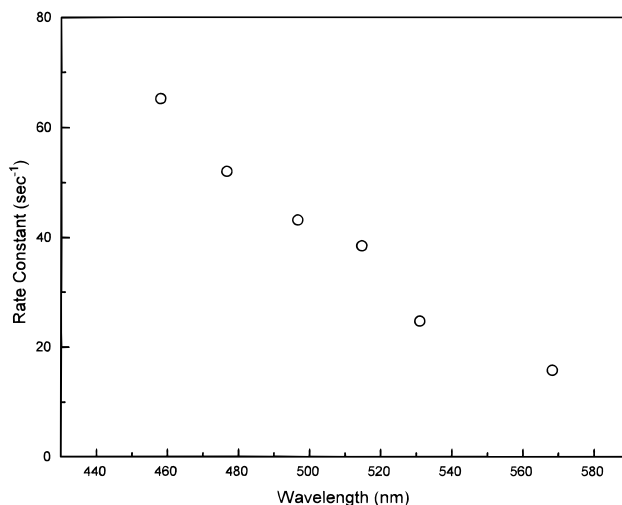

Figure 7. Plot of the photochemical rate constant derived from the data shown in Figure 6 as a function of excitation wavelength.

wavelength. Their trend suggests that the photodesorption is initiated by an absorption with considerable cross section in the visible and increasing toward the blue.

The absorption spectrum of samples of the colloid solution before and after the addition of 4vba is shown in Figure 8. Superimposed on it are points representing the relative SERS intensity of the strong 4vba band at 1606 cm^{-1} measured from an early (in fact the second) spectrum in the series of spectra used to determine the kinetics of photodesorption as a function of wavelength, i.e., from a spectrum in which the effect of photodesorption was negligible. The points, therefore, represent the relative SERS enhancement with respect to the CCl$_4$ intensity standard. By referring the intensity of the SERS bands to that of CCl$_4$, one also factors out (approximately) the ν^4 term characterizing Raman scattering. Hence, the data plotted in Figure 8 are a measure of the true, relative enhancement. The measured relative enhancement increases toward the red as expected for fractal colloidal aggregates.[17] The absorption spectrum of the aggregated colloid also lies in the region where the SERS intensity is high. Specifically, there seems to be little enhancement in the region of the spectrum where single colloidal particles absorb. Since the enhancement increases toward the red while the value of the rate constant increases toward the blue, we can assume that localized surface plasmon (LSP)
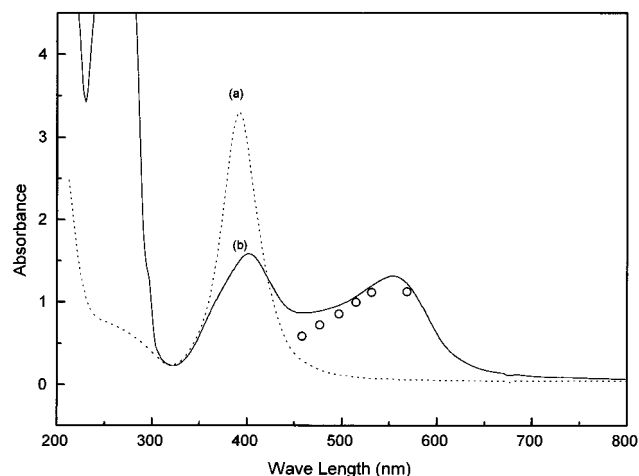
Figure 8. Portion of the UV—vis absorption spectrum (a) of silver colloid and (b) of 4-vinylbenzoic acid adsorbed on silver. The circular points indicate the relative SERS enhancement, in arbitrary units, plotted against the excitation wavelength.

absorptions are not involved in the photoprocess resulting in the desorption of 4vba.

Previously we suggested that the surface bonding of the form of 4vba which photodesorbs occurs largely through the π electrons of the benzene ring. The "spectrum" of the photochemical rate constant shown in Figure 7 does not lead to a unique mechanism of photodesorption. The field of surface photochemistry is very well established, and several possible schemes for photodesorption that might be applicable in our case have been proposed in other contexts.[18] One that is particularly plausible for our case is the so-called hot-electron model[19] in which an electron is excited from near the Fermi level of the metal to unoccupied levels in the conduction band that are degenerate with unoccupied levels of the metal—adsorbate complex. In this way antibonding states of the metal—adsorbate bond are populated, leading to a severe reduction of the metal—adsorbate bond order leading to facile desorption. This model is consistent with an absorption in the visible or near-ultraviolet leading to the observed photoprocess. Following arguments elaborated in ref 8, one can show that the magnitude of the work function of silver and the ionization potential of most aromatics are such as to locate a large number of normally unfilled molecular states in the ~4 eV region between the Fermi energy and the vacuum level. Hence, metal to (adsorbed) molecule transitions with energies in the visible and near-ultraviolet should be abundant. Some of them could be of the type that would result in the weakening of the metal—adsorbate bond.

Conclusions

4-Vinylbenzoic acid adsorbs on silver colloid surfaces in one of two forms: one of which photodesorbs under the influence of visible illumination and the other which does not. The photodesorption rate is large in the visible region and increases toward the blue, in contrast to the SERS enhancement which increases toward the red. Hence, the photodesorption mechanism does not involve localized surface plasmon excitation. The observed trend in the photodesorption rate constant implies that the process is initiated by a metal to molecule charge-transfer transition.

References and Notes

(1) Nitzan, A.; Brus, L. E. *J. Chem. Phys.* **1981**, *74*, 5321; **1981**, *75*, 2205.

(2) Das, P.; Metiu, H. *J. Phys. Chem.* **1985**, *89*, 4680.

(3) Wolkow, R. A.; Moskovits, M., *J. Chem. Phys.* **1987**, *87*, 5858

(4) Blue, D.; Helwig, K.; Moskovits, M.; Wolkow, R. *J. Chem. Phys.* **1990**, *92*, 4600.

(5) Goncher, M.; Parsons, C. A.; Harris, C. B. *J. Chem. Phys.* **1984**, *88*, 4200.

(6) (a) *Surface-Enhanced Raman Scattering;* Chang, R. K., Furtak, T. E., Eds.; Plenum: New York, 1982. (b) Moskovits, M. *Rev. Mod. Phys.* **1985**, *57*, 783.

(7) Suh, J. S.; Moskovits, M.; Shakhesemampour, J. *J. Phys. Chem.* **1993**, *97*, 1678.

(8) Suh, J. S.; Jang, N. H.; Jeong, D. H.; Moskovits, M. *J. Phys. Chem.* **1996**, *100*, 805.

(9) Suh, J. S.; Jang, N. H.; Jeong, D. H. *Bull. Korean Chem. Soc.* **1994**, *15*, 819.

(10) Suh, J. S.; Jang, N. H.; Jeong, D. H.; Haslett, T. L.; Moskovits, M. To be published.

(11) Suh, J. S.; DiLella, D. P.; Moskovits, M. *J. Phys. Chem.* **1983**, *87*, 1540. Creighton, J. A. Reference 6a, p 315.

(12) *Mechanics*; Symon, K. R., Ed.; Addison-Wesley: Reading, MA, 1971.

(13) Jeong, Dae Hong, Study of Photochemical Reactions of Molecules Adsorbed on Silver Colloid Surfaces, M.Ed. Thesis, Seoul National University, 1995.

(14) Varsanyi, G. *Assignment for Vibrational Spectra of Seven Hundred Benzene Derivatives*; John Wiley & Sons: New York, 1974; Vol. 1 and references therein.

(15) Dollish, F. R.; Fateley, W. G.; Bentley, F. F. *Characteristic Raman Frequencies of Organic Compounds*; John Wiley & Sons: New York, 1974 and references therein.

(16) (a) Moskovits, M.; Suh, J. S. *J. Phys. Chem.* **1984**, *88*, 1293. (b) Suh, J. S.; Kim, J. To be published.

(17) Stockman, M. I.; Shalaev, V. M.; Moskovits, M.; Botet, R.; George, T. F. *Phys. Rev.* **1992**, *B46*, 2821.

(18) *Laser Spectroscopy and Photochemistry on Metal Surfaces*; Dai, H. L., Ho, W., Eds.; World Scientific: Singapore, 1994. Heyd, D. V.; Jensen, E. T.; Polanyi, J. C. *J. Chem. Phys.* **1995**, *103*, 461.

(19) Yoshinobu, J.; Guo, X.; Yates, Jr. J. T. *J. Chem. Phys.* **1990**, *92*, 7700.