# Effect of Surface Geometry on the Photochemical Reaction of 1,10-Phenanthroline Adsorbed on Silver Colloid Surfaces

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The surface-enhanced Raman scattering spectra and the photochemistry of 1,10-phenanthroline (phen) adsorbed on silver colloid were studied using a flow cell. Phen adsorbed on fresh colloid is found to undergo almost no photochemistry while the same molecule adsorbed on aged colloid appears to photodecompose to a species in which the C−N ring bond in one or both of the heterocycles is broken to produce a C≡N moiety that binds to the silver surface. The contrast in the behavior of the two colloids is attributed to the differing bonding geometries of the adsorbate in the two cases. In the fresh colloid phen appears to bind with its $C_2$ axis normal to the local surface while on the aged colloid the molecule seems to bind flat on the surface. This difference in bonding strategy is ascribed to the existence of many surface defects on the surface of the fresh colloid that are ideal sites for bidentate chelation. These defects presumably significantly decrease in number as the surface heals with time. The photoproduct which forms upon irradiating phen adsorbed on aged colloid is subsequently observed to photodesorb at a rate significantly less rapid than that of the photodecomposition reaction. Both reactions are found to be one-photon processes; hence, the large photoreaction cross section in the visible is likely due to a metal-to-molecule charge-transfer transition.

## Introduction

The possibility that molecules adsorbed on surfaces capable of producing surface-enhanced Raman spectra are also capable of undergoing enhanced surface photochemistry was proposed theoretically and observed experimentally.[1−5] Surface-enhanced Raman scattering (SERS) spectroscopy was shown to be a powerful technique for studying such surface chemical reactions on the surface of colloidal metal aggregates.[6−7] The change in the concentration of reagents and products could be followed by observing the time evolution of the SERS spectra of the adsorbed reagents and/or products. Because the observation time for SERS, even using multichannel detection, often exceeds 0.1 s for reasonable signal-to-noise ratios, a long duration compared to the inverse rates of most surface photochemical reactions, we developed a simple flow method[8,9] that effectively expands the observation rate by several orders of magnitude. This method was successfully used to study the photoreaction of phthalazine,[8] the photodesorptions of diiodobenzene[9] and 4-vinylbenzoic acid,[10] and the photoisomerization of maleic acid[11] adsorbed on silver colloid surface.

Silver sols have been the most heavily used substrates in SERS experiments. The most intense surface-enhanced effects occur in assemblies of highly interacting small metal particles such as the large fractal clusters formed by colloidal metal particles,[12] which have been aggregated by the addition of an adsorbate to the metal colloid solution.[13] Because silver is not a highly chemically reactive surface, most SERS studies involve rather weakly adsorbed species. As a result, issues concerning the reactivity of the silver colloid surface and the existence of special reactive sites arose only seldom in the SERS literature. Of course the possible role of atomic scale roughness[14] in the enhancement mechanism did receive considerable attention prompting some[15] to propose a 4-fold ionic site as the locus for intense SERS. That discussion, however, was not aimed at understanding the possible chemistry at the surface. When considering the chemical nature of the surface, the possibility must be considered that this nature might undergo changes as a function of time, especially soon after the creation of the colloid from its precursors when the structure and crystallinity of the colloidal particles are being established. These changes in colloid structure might, in turn, be reflected in the surface chemistry of these systems toward adsorbates. In principle, one might expect that very fresh colloid would have a far more defective surface than colloid that had been aged. This difference might lead to different bonding geometries for adsorbates bound to the two types of surfaces. Such differences, which have been noted from time to time, are investigated more systematically in this study.

The SERS of 1,10-phenanthroline (phen), used extensively as a chelating ligand, has already been reported. Cooney et al.[16] observed the carbonization of phen on Ag electrode surfaces by laser light; however, Hajbi et al.[17] claim that only a portion of the adsorbed phen carbonizes on the Ag electrode surface mainly during the $Ag^1$−$Ag^0$ oxidation−reduction process and that photographitization appears as a minor effect.

Here, we report the photochemical reaction of 1,10-phenanthroline adsorbed on fresh and aged silver colloid surfaces using the flow-cell method described in refs 8−10.

## Experimental Section

Silver sols were prepared as described previously.[18] Briefly, a 60 mL of $2 \times 10^{-3}$ M sodium borohydride solution was mixed with $22 \pm 2$ mL of a $1 \times 10^{-3}$ M silver nitrate solution. Some colloid solutions were kept sealed for approximately 2 months on a vibrationless table during which time the colloid remained a clear yellow solution with little aggregation. Most of the aged colloid solutions aggregated rapidly upon the addition of adsorbates (although some did not).

Two types of phen/colloid systems were prepared for these studies, one using the 2-month old colloid ("aged colloid") and

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a second using colloid prepared a few days before the photochemical experiment was carried out ("fresh colloid"). The same quantity, 5 mL of $1 \times 10^{-3}$ M aqueous phen solution, was added dropwise to 100 mL of either fresh or aged silver colloid. Upon addition of adsorbate the sample of aged colloid turned a reddish-yellow color, indicating a slight degree of aggregation, while the fresh colloid became deep red, indicating a greater extent of aggregation. The overall concentration of phen in both samples was $4.5 \times 10^{-5}$ M. Poly(vinylpyrroli-done) (PVP, MW 40 000) was added to the solution as a stabilizer, preventing further aggregation and eventual floccula-tion of the colloid. The final concentration of PVP in the solution was approximately 0.007% by weight. 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 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 Ar ion laser (Lexel Model 3000) or 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 operated with st-130 program. Kinetics was recorded as a function of laser power (20−50 mW) at 514.5 nm and as a function of laser wavelength fot the six visible (457.9−568.2 nm) laser lines with 20 mW laser power at the sample position. The relative Raman intensities measured with the different laser lines were calibrated using $CCl_4$ as a standard. In order to check the extent of colloid aggregation, UV−vis spectra of the colloid samples were recorded using a Varian Cary 3 UV−vis spectrophotom-eter.

**Flow Kinetics.** The basic idea behind the techniques takes advantage of the fact that the poiseuille flow through a capillary is proportional to the pressure head feeding the tube. Hence, if a reservoir empties through a capillary, the flow rate will diminish smoothly with time. If only a small spot on the capillary is illuminated by the laser, then the residence time of a photoreagent molecule will be brief and that exposure time will increase as the flow rate decreases. A detailed discussion relating to the flow cell is contained in ref 8. Here we refine that derivation by considering in greater detail the expression used for the exposure time. The flow rate in the flow cells can be written as[19]

$$F = -A_{gc}\frac{dh}{dt} = ch \qquad (1)$$

where $A_{gc}$ is the cell cross sectional area of the cylindrical reagent reservoir, $h$ the instantaneous height of reagent solution in the reservoir, and $c$ a constant. Solving this equation gives the height of solution in the reservoir as

$$h = h_0 \exp(-t/\tau_0) \qquad (2)$$

where $h_0$ is the initial height and $\tau_0 = A_{gc}/c$. Hence the flow rate is given by

$$F = -A_{gc}\frac{dh}{dt} = (A_{gc}h_0/\tau_0)\exp(-t/\tau_0) \qquad (3)$$

The volume decrease in the cylindrical reagent reservoir equals its increase in the capillary;

$$-A_{gc}dh = A_c d\chi \qquad (4)$$

where $A_c$ is the cross sectional area of the capillary tube using a Raman cell, and $\chi$ the distance from the top of laser beam spot in the direction of flow to any position on the laser beam spot. By substituting $dh$ from eq 3 and rearranging, $d\chi$ becomes

$$d\chi = (A_{gc}h_0/A_c\tau_0)\exp(-t/\tau_0)dt \qquad (5)$$

Assume that the time after the flow is started when a molecule enters the edge of the laser beam ($\chi = 0$) is $t - t'$ and by time t the same molecule has flowed to location $\chi$ in the beam. Time, $t'$, therefore, corresponds to the laser exposure time ($t_{ex}$). Intergrating both sides of the eq 5 from 0 to $\chi$ and from $t - t'$ to t, respectively, and then rearranging produces the following expression for the exposure time[20]

$$t_{ex} = \tau_0\ln\{[A_c\chi/(A_{gc}h_0)]\exp(t/\tau_0)+1\} \qquad (6)$$

For simplicity, we have assumed the laser beam to have a square cross section and have ignored its Gaussian profile. The effects of these approximations have been discussed previously[8] and shown not to lead to serious errors in the seminal features of the kinetics affecting only the absolute but not the relative values of the photochemical rate constants determined. Since all of our conclusions will be drawn from the relative values of the rate constants, this approximation is tolerable.

We will show later that the photochemical reaction of phen adsorbed on silver colloid surfaces proceeds stepwise through an initial photodecoposition followed by a slow photodesorption of the photoproduct.

$$A + n \text{ photons} \xrightarrow{k_1} B + m \text{ photons} \xrightarrow{k_2} C$$
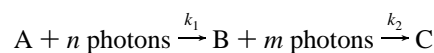
where A, B, and C represent the reagent, photoproduct and desorbed photoproduct, respectively, and $k_1$ and $k_2$ are, respec-tively, the rat constants of the photodecomposition and photo-desorption processes. The time rates of change of A and B (the concentrations of A and B will be denoted by $A$ and $B$) are given by

$$dA/dt_{ex} = -k_1A \qquad (7)$$

$$dB/dt_{ex} = k_1A - k_2B \qquad (7')$$

Which have the following solutions:

$$A = A_0e^{-k_1t} \qquad (8)$$

$$B = \frac{k_1A_0}{k_2 - k_1}(e^{-k_1t_{ex}} - e^{-k_2t_{ex}}) \qquad (8')$$

The rate constants $k_1$ and $k_2$ will, in general, depend on the laser intensity $I$ as $k_1 = a_1I^n$ and $k_2 = a_2I^m$, where $n$ and $m$ are the apparent numbers of photons required to initiate these photo-reactions and $a_1$ and $a_2$ are wavelength-dependent quantities proportional to the absorption cross section.

Since the photoproduct desorbed from the silver surfaces does not contribute to the SERS signal, all SERS bands will belong to phen and its initial photoproduct. Hence, in general, the
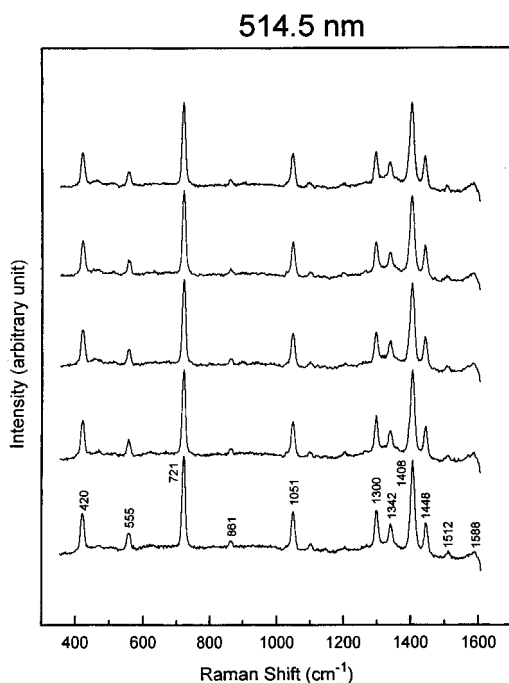
Photochemical Reaction of 1,10-Phenanthroline

*J. Phys. Chem. B, Vol. 101, No. 41, 1997* **8281**



**Figure 1.** The 2nd, 50, 100, 150, and 200th SERS spectra (bottom to top) of 1,10-phenanthroline adsorbed on *fresh* silver colloid of a 200 spectrum series recorded using multichannel detection and 514.5 nm Ar$^+$, 20 mW laser excitation. The spectra were recorded in a flow cell.

observed SERS intensity of a band is given by

$$I_{obs} = I\sigma_A A + I\sigma_B B + \text{base line} \quad (9)$$

where $\sigma_A$ and $\sigma_B$ are the Raman cross sections of phen and its photoproduct, respectively.

The SERS intensity originates from all of the molecules illuminated by the laser spot. These will have been exposed to the laser beam for varying lengths of time depending on location of the molecule within the laser beam: those molecules that have just entered the beam will have been irradiated for a short time while those about to exit the beam will have been exposed for the longest time. Hence the concentrations of A and B in eq 9 must be averaged over this varying exposure time. If the side of the square representing the laser spot is $L$, the average concentrations of A and B in the illuminated portion of the capillary are given by

$$\bar{A} = \frac{1}{\tau} \int_0^\tau A \mathrm{d}t_{ex} = \frac{A_0}{k_1 \tau}[1 - \exp(-k_1\tau)] \quad (10)$$

$$\bar{B} = \frac{1}{\tau} \int_0^\tau B \, \mathrm{d}t_{ex} = \frac{A_0}{k_2 \tau} - \frac{k_1 A_0}{(k_2 - k_1)\tau}\left[\frac{e^{-k_1\tau}}{k_1} - \frac{e^{-k_2\tau}}{k_2}\right] \quad (10')$$

where $\tau = \tau_0 \ln\{[A_c L/(A_{gc} h_0)] \exp(t/\tau_0) + 1\}$.

And the observed Raman intensity of a SERS band is

$$I_{obs} = I\sigma_A \bar{A} + I\sigma_B \bar{B} + \text{base line} \quad (11)$$

This is the equation which will be used to analyze the time evolution of phen adsorbed on the aged silver colloid surface.

## Results and Discussion

A representative series of SERS spectra of phen adsorbed on fresh and aged silver colloids recorded using the flow cell are shown in Figures 1, 2 and 3−6, respectively. For most runs 200 spectra were collected sequentially in 5 s intervals. The
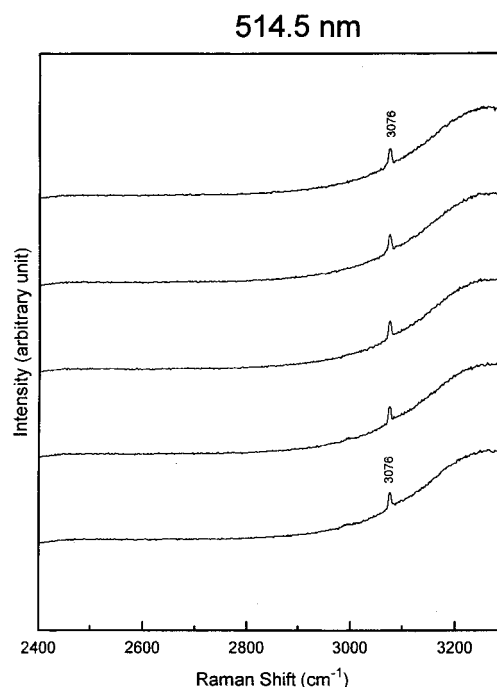


**Figure 2.** Same as in Figure 1 except for the aromatic CH stretching region of the spectrum.
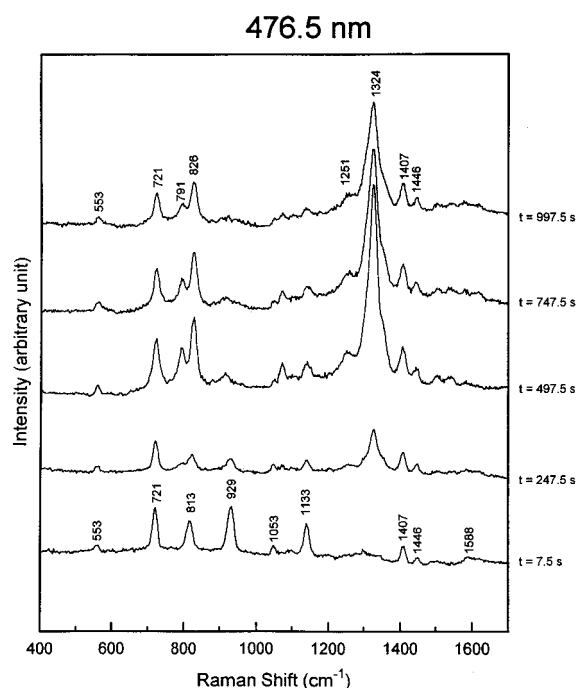


**Figure 3.** The 2nd, 50, 100, 150, and 200th SERS spectra (bottom to top) of 1,10-phenanthroline adsorbed on *aged* silver colloid of a 200 spectrum series recorded using multichannel detection and 476.5 nm Ar$^+$, 20 mW laser excitation. The spectra were recorded in a flow cell.

spectra reported in Figures 1−6 are (bottom to top) the 2nd, 50, 100, 150 and 200th spectra corresponding to mean times of 7.5, 247.5, 497.5, 747.5, and 947.5 s after the flow was initiated. The exposure time also increases as a function of time such that the average exposure times for the displayed spectra are $3.48 \times 10^{-5}$, $2.09 \times 10^{-3}$, $1.49 \times 10^{-1}$, 9.05, and 96.5 s, respectively. In Figures 1−6 the base lines were displaced by equal intervals for clarity. The background signals did not increase substantially with time.

The SERS spectra of phen adsorbed on fresh silver colloid and excited with 20 mW of 514.5 nm Ar$^+$ laser light are shown
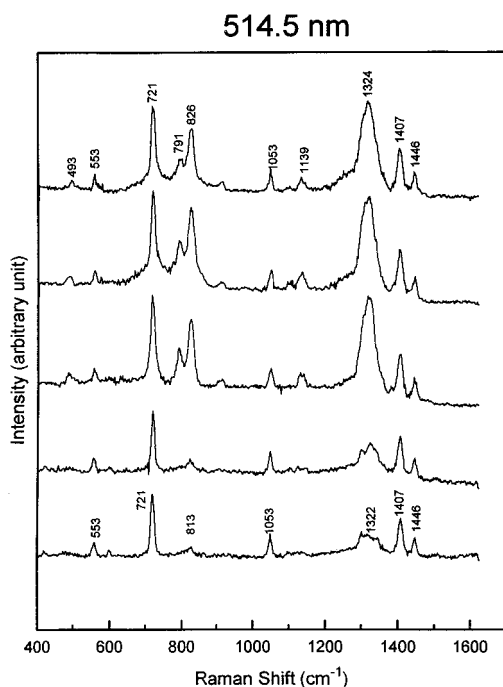
## 514.5 nm



**Figure 4.** Same as in Figure 3 except with 20 mW of 514.5 nm Ar$^+$ laser excitation.
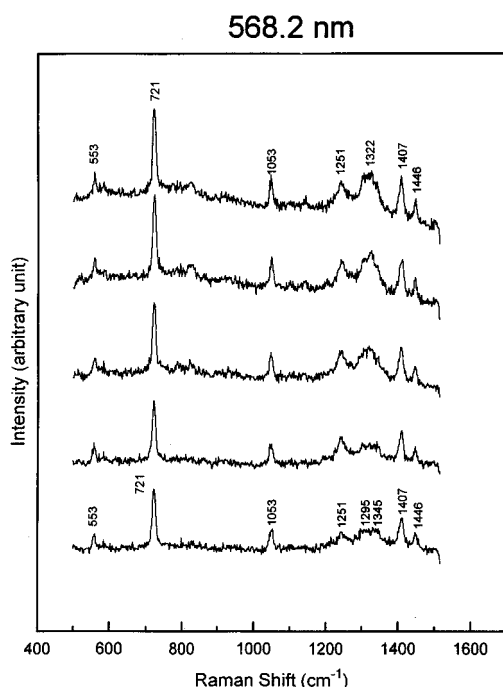
## 568.2 nm



**Figure 5.** Same as in Figure 3 except with 20 mW of 568.2 nm Kr$^+$ laser excitation.

in Figure 1. No spectral change is observed with increasing exposure time for any of the laser wavelengths, ranging from 457.9 nm to 568.2 nm, used. The strong bands observed at 420, 555, 721, 861, 1051, 1095, 1300, 1342, 1408, 1448, 1512, and 1588 cm$^{-1}$ are all assignable to in-plane, in-phase (A$_1$) modes of phen.[21] The peak positions and their vibrational assignments are summarized in Table 1. The strong band at 3076 cm$^{-1}$ in Figure 2 is due to aromatic CH stretching which is also an A$_1$ mode. A strong aromatic CH stretching band in the SERS spectrum suggests that phen is adsorbed in a "standing up" orientation on the surface:[22] that is, the molecule chelates a surface site in such a way that its $C_2$ axis lies more or less parallel to the local normal to the surface. Because no photoreaction was observed for the molecule adsorbed on fresh
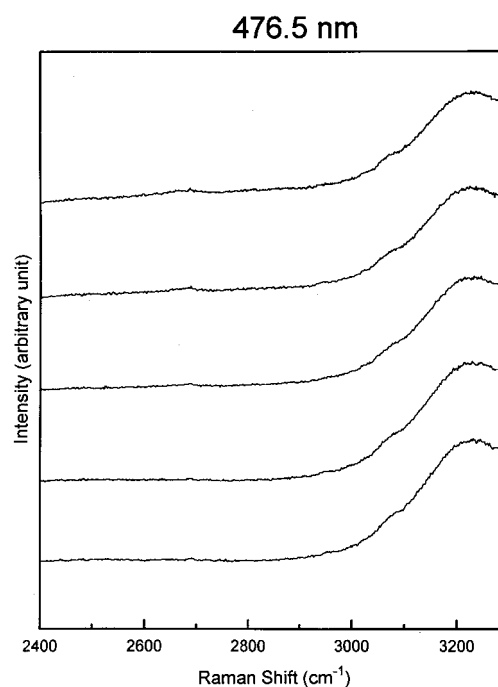
## 476.5 nm



**Figure 6.** Same as in Figure 3 except for the aromatic CH stretching region of the spectrum.

**TABLE 1: Assignments of Spectral Data for 1,10-Phenanthroline**

| FT-Raman (solid) | SERS | | | assignment[c] |
| | fresh colloid | aged colloid | | |
| | | 2nd[a] | 200th[b] | |
|---|---|---|---|---|
| 411 | 420 | | | $\nu2(A_1)$ |
| 508 | | | | $\nu52(B_1)$ |
| 552 | 555 | 553 | 553 | $\nu3(A_1)$ |
| 711 | 721 | 721 | 721 | $\nu4(A_1)$ |
| | | | 791[d] | $\nu NCCC^d$ |
| | | 813 | | $\nu60(A_2)$ |
| | | | 826[d] | $\nu NCCC^d$ |
| 856 | 861 | | | $\nu5(A_1)$ |
| | | 929 | | $\nu58(A_2)$ |
| 1036 | 1051 | 1053 | | $\nu6(A_1)$ |
| 1096 | 1095 | | | $\nu7(A_1)$ |
| | | 1133 | | $\nu31(B_2)$ |
| | | | 1251[d] | unknown |
| 1294 | 1300 | | | $\nu12(A_1)$ |
| | | | 1324[d] | $\nu C{=}N^d$ |
| 1344 | 1342 | | | $\nu13(A_1)$ |
| 1404 | 1408 | 1407 | 1407 | $\nu14(A_1)$ |
| 1446 | 1448 | 1446 | 1446 | $\nu15(A_1)$ |
| 1502 | 1512 | | | $\nu16(A_1)$ |
| 1562 | | | | $\nu39(B_2)$ |
| 1587 | 1588 | 1588 | | $\nu18(A_1)$ |
| 1606 | | | | $\nu40(B_2)$ |
| 3063 | 3076 | | | $\nu22(A_1)$ |

[a] Referred to the 2nd spectrum observed by 476.5 nm. [b] Referred to the 200th spectrum observed by 476.5 nm. [c] Referred from ref 21a: A$_1$, in-plane, in-phase; A$_2$, out-of-plane-in-phase; B$_1$, out-of-plane-out-of-phase; B$_2$, in-plane, out-of-phase. [d] Photoproduct bands.

colloid, we conclude that phen adsorbed "standing up" on the surface of the silver colloid does not undergo photochemistry.

On the contrary, the SERS spectra of phen adsorbed on aged silver colloid change dramatically with increasing laser exposure time as shown in Figures 3−5, where the time evolution of the SERS spectra of phen adsorbed on aged colloid are shown upon irradiation with 476.5 nm and 514.5 nm Ar$^+$ and 568.2 nm Kr$^+$ laser radiation at 20 mW. Measurements were also carried out with 457.9, 496.5, and 530.9 nm excitation but not shown. In all of these SERS spectra, even the spectra recorded after the

shortest exposure times before a great deal of photochemistry could have taken place the spectra are already different compared to those recorded with fresh colloid. For example, the strong band at 420 cm$^{-1}$ in the SERS spectrum of phen on fresh colloid is very weak, and the aromatic CH stretching band near 3070 cm$^{-1}$ is also very weak appearing only as a weak shoulder (Figure 6) implying that on aged colloid phen lies rather flat with respect to the local silver surface.[22] That is, the surface geometry of phen on aged colloid surface differs from that on fresh colloid.

The SERS spectra of phen adsorbed on aged colloid also show some spectroscopic differences according to the excitation wavelength used. For example, spectra excited with 476.5 nm Ar$^+$ laser (see Figure 3), contain three bands at 813, 926, and 1133 cm$^{-1}$ which do not appear, or are very weak, in the early (short irradiation time) spectra excited with 514.5 or 568.2 nm light. For example, the band at 813 cm$^{-1}$ is very weak in the spectrum excited with 514.5 nm laser (lowest-most spectrum in Figure 4).

The bands at 813 and 929 cm$^{-1}$ are assigned to out-of-plane, in-phase (A$_2$) modes of phen while the band at 1133 cm$^{-1}$ is due to an in-plane, out-of-phase (B$_2$) vibration.[21] The changes in intensity of these bands with excitation wavelength is almost certainly an example of so-called surface selection rules for SERS.[23] The operation of these "selection rules" is particularly evident with the aged colloids because they aggregate only slightly as evidenced by the fact that the UV–vis spectra of the aggregated colloids do not have the broad absorption feature covering the entire visible spectrum, which is characteristic of aggregated fresh colloid, but rather only a weak extra shoulder centered at approximately 470 nm to the red of the band at 390 nm due to absorption by isolated colloid particles. In ref 23 it was shown that, as the excitation becomes less resonant with the surface plasmon absorption, nontotally symmetric modes such as A$_2$ and B$_2$ modes become weak. This loss of resonance is achieved very quickly with the aggregated aged colloid as the excitation wavelength moves toward the red but cannot be easily achieved with aggregated fresh colloid.

The spectral changes shown in Figure 3 indicate two types of time evolution for the bands observed. The first, shown, for example, by the band at 929 cm$^{-1}$, decreases monotonically with increasing laser exposure time. These bands undoubtedly belong exclusively or almost exclusively to the original phen reagent molecules. The second, increases in intensity at first then decreases with increasing exposure time. The bands at 791, 826, 1251, and 1324 cm$^{-1}$ are of the second type. We suggest that these bands are due to a photoproduct or products whose surface concentration first increases then decays due to photodesorption. One band (721 cm$^{-1}$) shows a more complex time evolution that can be shown to be a linear combination of the two. Hence this band has significant contributions from both reagent and photroproduct, an interpretation that is further strengthened by subtle changes in the band contour as a function of time.

The strong band at 1324 cm$^{-1}$ can be assigned to a C=N stretching vibration ($\nu_{C=N}$)[24] suggesting that phen photodecomposes to a photoproduct possessing a −C=N bond which, due to its great enhancement, is in close contact with the surface. Although very weak, this $\nu_{C=N}$ photoproduct band is seen clearly even after short irradiation times. The bands at 791 and 826 cm$^{-1}$ are possibly due to vibrational modes associated with $\nu_{NCCC}$ in the photoproduct.[24] The origin of the photoproduct band at 1251 cm$^{-1}$ is unclear.

Although the conversion of phen to adsorbed carbon on an Ag electrode was previously reported[16,17] no evidence of this reaction is observed in our experiment; specifically, the broad band centered at approximately 1600 cm$^{-1}$ due to disordered graphite[16,17] is not observed in any of our spectra. This implies that in our experiments the photochemistry produces relatively simple photoproducts in which a great deal of the molecular integrity of the original phen molecule is preserved. Specifically, our results imply that at least one CN bond in phen breaks during the photoreaction producing a C=N group. Moreover, only phen $\pi$-bonding to the silver surface with its plane more or less parallel to the local surface photoreacts. Such a surface orientation seems to be the favored one on aged colloid whose surface is presumably more planar and with fewer surface defects than that of the fresh colloid. It is presumably the surface defects serving as chelating sites that are responsible for the upright bonding geometry of phen adsorbed on fresh colloid.

The geometry of the photoproduct cannot be unequivocally deduced on the basis of the SERS spectra. However some geometrical clues can be deduced from the spectra. The presence of a C=N group as evidenced by the stretching vibration at 1324 cm$^{-1}$ might come about as a result of the cleavage of bonds C$_{13}$−N and/or C$_{14}$−N which are relatively weak compared the C−C bonds.
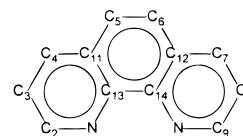


If only one of these C-N bonds is broken, the phen becomes a 7-substituted quinoline, which might bind to the surface in one of two possible ways (see **I** or **II**). If the quinoline ring is adsorbed directly, either lying down or standing up, on the surface as in **I**, one would expect to see SERS bands associated with quinoline ring modes. This is not observed. Therefore, it is unlikely that the photoproduct adopts this adsorption geometry. Another possibility is that the nitrogen atom arising from the broken bond is adsorbed on the surface as in **II** and that the quinoline ring is not adsorbed directly on the surface. In this case, a strong $\nu_{C=N}$ mode is expected in the spectrum while bands associated with quinoline ring modes should be weak in the SERS spectrum because the quinoline part of the ring is remote from the surface. The spectral features expected with bonding geometry **II** is closer to what we observe than what is expected in a SERS spectrum of a structure interacting with the surface as in **I**.


(**I**)                (**II**)
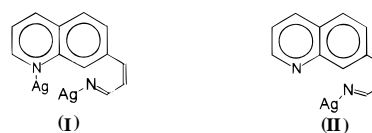
If both of the C-N bonds are broken, a photoproduct will result with the structure of a *p*-disubstituted benzene (**III**).


(**III**)
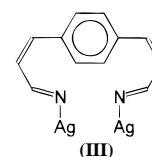
The nitrogen ends of the two C=N groups produced could bind to the surface in such a way that the benzene ring is sufficiently displaced from the surface so as to make its vibrational modes weak in the resulting SERS spectrum. Only the $\nu_{C=N}$ modes
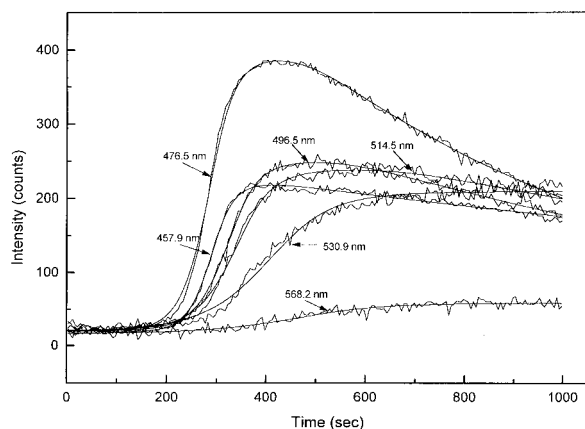
**Figure 7.** Time evolution of the SERS intensity of the 1321 cm$^{-1}$ band excited with 514.5 nm Ar$^+$ laser light. Jagged lines are experimental data. Smooth lines are fitted curves. The laser power used is (top to bottom) 50, 40, 30, and 20 mW.

are expected to be strong as observed. The SERS spectra alone cannot distinguish between **II** and **III** as possible photoproducts. If **III** is the photoproduct, then the scission of the two C−N bonds occurs following the absorption of a single photon. Additionally, the rupture of the two bonds must occur either simultaneously or sufficiently rapidly one after the other to make impossible the observation of the intermediate in which only the first C−N bond is broken. The photon energy of a single visible photon is insufficient to break two C=N bonds, however, the formation of two Ag−N surface bonds might more than make up the energy difference. Nevertheless, the energy barrier to the simultaneous rupture of both C=N bonds may still be large compared to the energy of a single visible photon. This fact together with the fact that we see the desorption of the photoproduct—a two-site bonded structure such as **III** would make the desorption process more difficult—encourages us to lean towards a species such as **II** rather than **III** as the photoproduct. However, the precise nature of the photoproduct is unknown.

Figure 7 shows the time evolution of the SERS intensity of the photoproduct band at 1324 cm$^{-1}$, irradiated with 514.5 nm Ar ion laser light. The four traces represent differing laser intensities ranging from 20 to 50 mW. The jagged lines are experimental data and the smooth lines are recalculated curves after fitting the data to eq 11 using eq 10′ and $\tau$. We assumed $\sigma_A = 0$ since there is no reagent contribution at 1324 cm$^{-1}$. The best fit was obtained with $a = 17.5$, $b = 0.15$ mW$^{-1}$ s$^{-1}$; $n = 0.95$, $m = 1.0$. These constants refer to $k_1 = al^n$ and $k_2 = bl^m$. The four curves in Figure 7 were fit simultaneously using a single set of parameters. A value of $\tau_0 = 58.6$ s was returned by the fit. The experimental data could not be fit with $n$ and $m$ equal to or in the vicinity of 2. We conclude that the photodecomposition of phen on the aged Ag colloid surface and the subsequent photodesorption of the photoproduct are each initiated by one-photon processes.

The photochemical rate constant is found to be wavelength dependent in the visible region. The time evolutions of the 1324 cm$^{-1}$ band following irradiation of the colloid with six excitation wavelengths is shown in Figure 8. With 20 mW laser power, the values of the rate constant, $k_1$, for the photodecomposition obtained by fitting eq 11 to the data shown in Figure 8 are found to be 0.0, 68.5, 343.3, 501.2, 732.5, and 646.6 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 values for the rate constant $k_2$ for the photodesorption step were obtained simultaneously as 0.0, 0.34, 4.1, 8.6, 17.0, and 17.8 s$^{-1}$, respectively. The rate of photodesorption is found to be much slower than that of
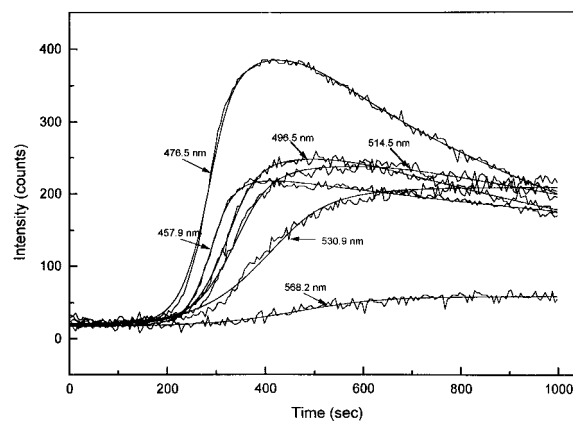


**Figure 8.** Time evolution of the SERS intensity of the 1321 cm$^{-1}$ line excited with several Ar$^+$ and Kr$^+$ laser lines. The laser power was 20 mW in all cases. Intensities were calibrated against the Raman spectrum of CCl$_4$, and the base lines were removed.
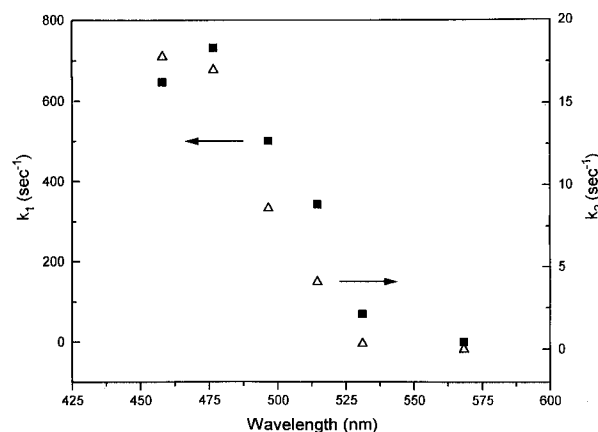


**Figure 9.** Plot of the photodecomposition $k_1$ and photodesorption $k_2$ rate constants derived from the data shown in Figure 8 as a function of excitation wavelength.

photodecomposition. These rate constants are plotted in Figure 9 as a function of excitation wavelength. Although differing markedly in magnitude, both rate constants increase toward the blue. Although $k_1$ appears to have a maximum at approximately 470 nm, because the maximum is indicated by a single point the extent of further increase on going even farther into the blue is not clear from the data. Nevertheless, the rate of increase of the spectra of the two rate constants appears to be abating in the vicinity of the blue limit of our experiment indicating that the band maximum associated with this process is likely not much bluer than 450 nm. With 550 nm or longer wavelength essentialy no photoreaction takes place.

Phen has no absorptions in visible or near UV; however, the action spectrum of the two photochemical rates suggest an absorption in or near the visible. This type of observation was previously[8] attributed to the presence of a metal-to-adsorbate charge transfer process that essentially produces an excited anion of the adsorbed molecule which then undergoes the chemical transformation to the photoproduct. Interestingly, the reaction appears to be initiated only in phen molecules laying flat on the surface. This might supply an important clue regarding the state of phen or its anion which is involved in the photoreaction.

## Conclusions

1,10-Phenanthroline (phen) adsorbed on fresh colloid is found to undergo almost no photochemistry while the same molecule adsorbed on aged colloid appears to photodecompose to a species in which the C−N ring bond in one or both of the

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heterocycles is broken to produce a C=N moiety that binds to the silver surface. The contrast in the behavior of the two colloids is attributed to the differing bonding geometries of the adsorbate in the two cases. In the fresh colloid phen appears to bind with its $C_2$ axis normal to the local surface while on the aged colloid the molecule seems to bind flat on the surface. This is ascribed to the possibility that the fresh colloid has innumerable surface defects that are ideal sites for bidentate chelation. These defects presumably decrease in number significantly as the surface heals with time. The photoproduct which forms upon irradiating phen adsorbed on aged colloid, is observed to photodesorb. The photodissociation rate is found to be significantly faster than the rate of photodesorption. Both reactions are found to be one-photon processes; hence, the large absorption cross section in the visible is likely due to a metal to molecule charge-transfer transition.

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