

Photodecomposition of Diazanaphthalenes Adsorbed on Silver Colloid Surfaces

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The surface photoreactivity of four diazanaphthalenes (phthalazine, cinnoline, quinazoline and quinoxaline) adsorbed on aqueous colloidal silver was studied by following the time evolution of the SERS spectra of their photoproducts with laser irradiation time in a flow cell. All of these molecules were found to photodecompose through the cleavage of N=N or N–C bonds of the heterocycle while the benzene ring remained intact. Cinnoline, which adsorbed as a σ -complex “standing up” on the surface, showed very little reactivity. Quinazoline at high surface concentrations was also found to form a σ -complex (likely due to the fact that more adsorbate could be packed in that orientation). It, too, showed essentially no surface photoreactivity. To the contrary, quinazoline at low surface concentrations formed a π -complex, “lying down” on the surface. In this orientation quinazoline photoreacted rapidly. For quinoxaline, two distinct photoprocesses were observed depending on the presence or absence of coadsorbed chloride ion on the surface. The wavelength response of the formation rate of these products in the absence and presence of chloride suggests that the coadsorbed halide modifies the electronic properties (probably locally) of the silver. Multiple photoproducts were observed to be formed in several cases. Although an unequivocal identification of the products was not possible, plausible assignments were suggested on the basis of the observed vibrational spectra.

Introduction

Enhanced surface photochemistry of molecules adsorbed on surfaces capable of producing surface-enhanced Raman is now a well-established and well-studied phenomenon.^{1–5} Surface-enhanced Raman scattering (SERS) spectroscopy⁶ is a powerful technique for following surface chemical reactions because relatively low surface concentrations of the reagents, the products and, sometimes, even of the reaction intermediates can be detected using SERS. Previously we reported on a simple flow method^{7,8} that permits relatively fast surface photochemical reactions of molecules adsorbed on silver colloid surfaces to be studied using SERS as a probe. This method was used successfully to study the photodecomposition,^{8,9} photoisomerization,¹⁰ and photodesorption^{7,11} of molecules adsorbed on silver colloid surface.

The SERS spectra of several diazanaphthalenes adsorbed on silver under varying conditions have previously been reported.^{12–15} For example, the changes in the SERS spectra of those species produced by the coadsorption of anions,^{13–15} resulting from varying the concentration,¹⁴ excitation wavelength,¹² and electrode potential¹³ have been studied. The observed spectral changes were interpreted in terms of differing molecular orientation^{13–15} or in terms of surface selection rules.¹² Recently, the SERS spectrum of phthalazine adsorbed on silver colloid was reexamined on the basis of results obtained in a flow cell,

and the conclusion was drawn⁸ that many of the spectroscopic changes attributed to the various causes listed above^{12–14} were, in fact, due to the surface photodecomposition of phthalazine. It, therefore, appears necessary to reexamine the SERS spectra of the isomers of phthalazine to gauge the extent to which the products of surface-enhanced photodecomposition play a role in producing the variety of spectral features attributed to the parent molecule, as well as to attempt to understand the photochemical dynamics that occur. In this paper we examine the photochemistry and reexamine the SERS spectra of cinnoline, quinazoline, and quinoxaline adsorbed on the colloidal silver using a flow cell.

Experimental Section

The preparation method of the silver sols was described previously.¹⁶ Briefly, 60 mL of a 2×10^{-3} M sodium borohydride solution were mixed with 22 ± 2 mL of a 1×10^{-3} M silver nitrate solution. Sols with time-independent properties were obtained only after the sols were aged for approximately one month. Sample solutions of adsorbed phthalazine, quinazoline, and cinnoline on the silver colloid particles were prepared by adding aqueous phthalazine, quinazoline, and cinnoline dropwise to the colloid solution such that the final concentrations of phthalazine and cinnoline were 2.7×10^{-5} and 2.3×10^{-5} M, respectively. For quinazoline, samples with final overall adsorbate concentrations of 1.3×10^{-4} and 1.3×10^{-5} M were prepared with and without the addition of KCl. When chloride was added it was added to a final concentration of 1.3×10^{-4} M. For quinoxaline, two kinds of samples were prepared: one by adding 5 mL of 5×10^{-3} M aqueous quinoxaline dropwise to 100 mL of sol; the other by

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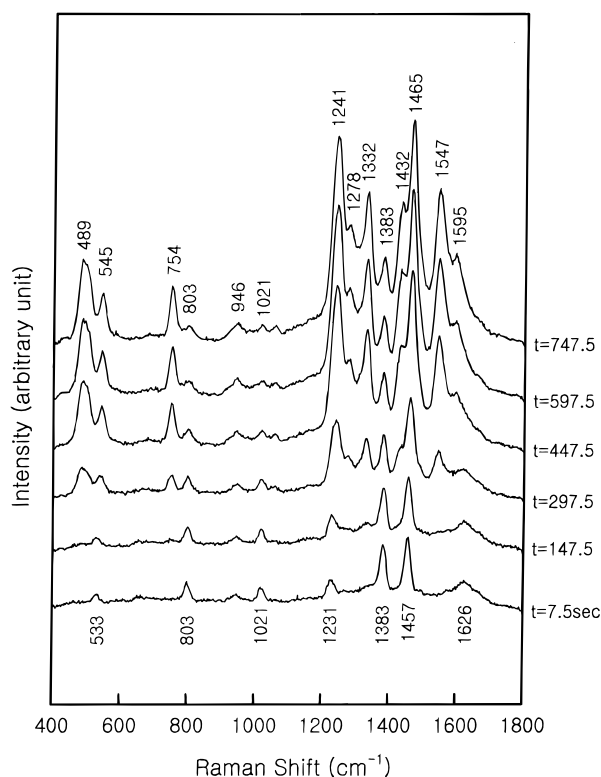


Figure 1. Six representative spectra out of a series of 150 spectra each (bottom to top) corresponding to progressively longer laser irradiation times for the system phthalazine adsorbed on aqueous colloidal silver. The mean irradiation times to which a molecule is exposed while its spectrum was recorded are 2.6×10^{-4} , 3.7×10^{-3} , 6.3×10^{-2} , 1.1, 16, and 109 s, respectively. (The spectra were recorded with 476.5 nm Ar⁺ laser excitation at 20 mW).

adding 0.3 mL of 0.1 M HCl or KCl before or after the addition of the quinoxaline to the silver sol. The overall concentration of quinoxaline was 2.2×10^{-4} M. The color of the colloid solutions changed from light yellow to purple upon the addition of the adsorbate. Poly(vinylpyrrolidone) (PVP, MW 40000) was added to all of the solutions as a stabilizer, preventing massive aggregation and the eventual flocculation of the colloid. The final concentration of PVP in the solution was approximately 0.007 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 instrumental setup has been described elsewhere.⁸ Surface-enhanced Raman scattering was excited focusing the beam of an Ar ion or Kr ion laser (Lexel Models 3000 and 3500) onto the glass capillary of the flow system. Spectra were recorded using a Spex 1887C Triplemate spectrometer equipped with multichannel charge-coupled device (CCD) detection and interfaced to an IBM personal computer. Raman intensities were calibrated against a liquid CCl₄ reference. To check the extent of colloid aggregation UV-visible spectra were recorded using a Varian Cary 3 UV-visible spectrophotometer.

Results and Discussion

A representative series of SERS spectra of phthalazine, quinoxaline, and quinoxaline adsorbed on aqueous silver colloid and recorded at various flow rates are shown in Figures 1 and 3–5. The different flow rates, in essence, represent different average laser irradiation times for a given adsorbate-covered colloidal cluster aggregate; the faster the flow rate the shorter the irradiation time.

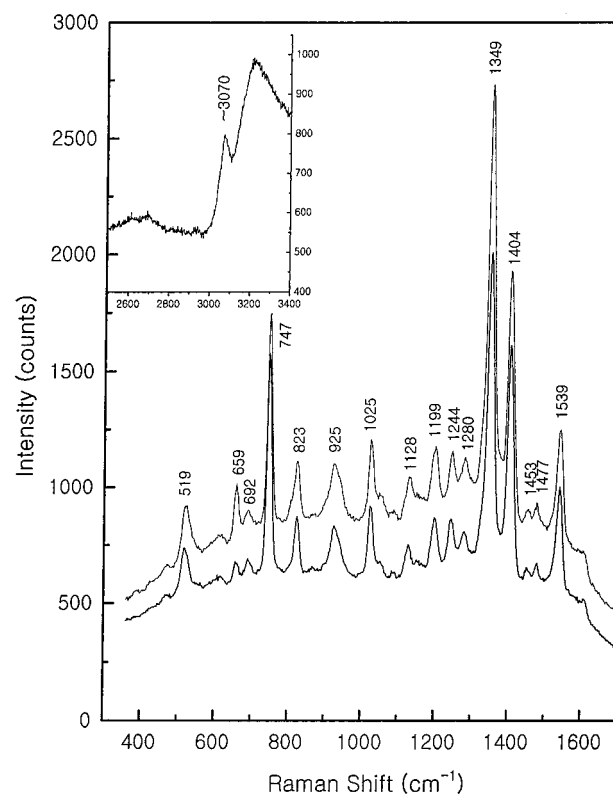


Figure 2. SERS spectra of quinoxaline adsorbed on silver colloid, without added Cl⁻ ion, recorded with fast flow (upper) and no flow (lower). 496.5 nm Ar⁺ laser excitation at 40 mW. The overall concentration of quinoxaline is 1.3×10^{-4} M.

The principle behind the operation of the flow cell is discussed in detail in ref 8. Briefly, an aqueous solution containing adsorbate-covered colloidal silver aggregates is allowed to empty out of the bottom of a cylinder through a capillary under the influence of gravity. As the cylinder empties the pressure head diminishes with time resulting in a flow rate that decreases with increasing time. By calibrating the flow rate the mean irradiation time could be calculated given the known dimensional parameters of the capillary and the laser beam, and making certain defensible assumptions. The spectra of phthalazine were previously reported⁸ and are shown here for comparison. For quinoxaline, the two series of spectra observed for samples prepared with and without added Cl⁻ ion are shown in Figures 4 and 5, respectively. For most runs 150 or 200 spectra were collected sequentially every 5 s. The spectra reported in Figure 1 are (bottom to top) the 2nd, 30th, 60th, 90th, 120th, and 150th spectra corresponding to 7.5, 147.5, 297.5, 447.5, 597.5, and 747.5 s after the flow was initiated. The spectra reported in Figures 3–5 are (bottom to top) the 2nd, 50th, 100th, 150th, and 200th spectra which correspond to 7.5, 247.5, 447.5, 747.5, and 997.5 s after the flow was initiated which, in turn, correspond to mean irradiation times of 6.6×10^{-4} , 0.061, 6.4, 145, and 391 s, respectively. The SERS spectra of quinoxaline adsorbed on silver with an overall adsorbate concentration of 1.3×10^{-4} M without added Cl⁻ ion are shown in Figure 2 recorded with fast flow and no flow.

The SERS spectra of cinnoline are shown in Figure 6. The bottom spectrum was recorded with fast flow analogous to the bottom-most spectra in Figures 1 and 3–5. The upper series of spectra were collected sequentially every 1 s from a sample contained in a capillary and continuously irradiated by the laser; i.e., without flow. The (bottom to top) 1st, 5th, 10th, and 50th spectra are shown.

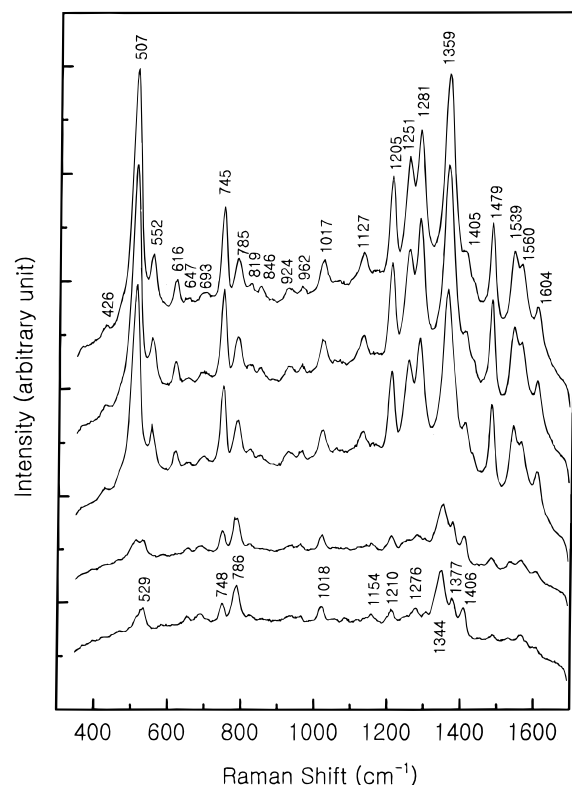


Figure 3. A representative series of spectra out of a total of 200 spectra each (bottom to top) corresponding to progressively longer laser irradiation times. The system was quinazoline adsorbed on aqueous colloidal silver *with* added Cl^- ion whose overall concentration was 1.3×10^{-4} M. The mean irradiation times to which a molecule is exposed while the spectra were recorded are 6.6×10^{-4} , 0.061, 6.4, 145, and 391 s, respectively.

In the aforementioned figures the baseline is displaced in equal intervals for clarity. In reality, the background signal did not decrease substantially with time. Although measurements were made with 457.9, 476.5, 496.5, 514.5, 530.9, and 568.2 nm excitation, only representative spectra excited with one of these laser lines are shown in the figures.

The bottom spectrum in each of the above figures, corresponding to the second spectrum in the series of 150 or 200 spectra, is rather simpler than those recorded with longer irradiation times. Those early spectra, recorded from samples exposed for only 6.6×10^{-4} s, are found to be almost identical regardless of excitation wavelength. Hence we interpret these to be the SERS spectra of the native adsorbate with little or no photochemistry having taken place. With increasing exposure time the SERS spectra become more complicated with several new bands appearing. (See Table 1 for a summary.) This suggests that the new bands belong to photoproducts produced from the adsorbed molecules. Product bands assignable to benzene ring vibrations appear to grow in most rapidly. For example, the band near 1590 cm^{-1} can be assigned to ν_{8a} , while the bands near 1480, 1270, 1070, 740, 610, and 550 cm^{-1} can be assigned to ν_{19b} , ν_3 , ν_1 , ν_4 , ν_{16a} , and ν_{6b} , respectively. (For band assignment and nomenclatures see ref 17.) The band at 634 cm^{-1} for the quinoxaline sample with added Cl^- ion is likely the ν_1 band of a substituted benzene whose frequency is very sensitive to the mass of the directly bonded substituent.¹⁷ For example, its frequency falls in the range $1030\text{--}1085\text{ cm}^{-1}$ for ortho-“light”-“heavy” compounds and $635\text{--}780\text{ cm}^{-1}$ for ortho-“light”-“light” substituted benzenes. The band near 1350 cm^{-1} is, therefore, assigned to ν_{CN} . The low-frequency band near 500 cm^{-1} would then be the bending mode of the

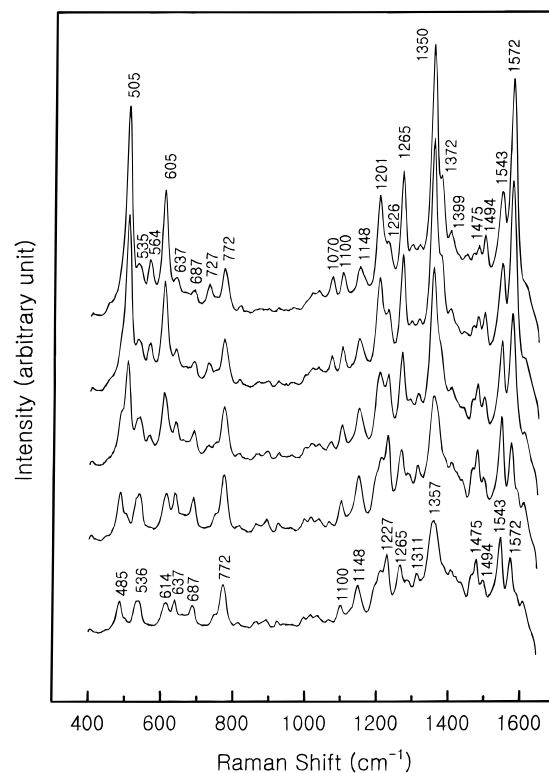


Figure 4. Five representative spectra out of a series of 200 each (bottom to top) corresponding to progressively longer laser irradiation times for the system quinoxaline adsorbed on silver colloid, with no added Cl^- ion. The mean irradiation times to which a molecule is exposed while its spectrum was recorded are 2.6×10^{-4} , 2.4×10^{-2} , 6.4, 145, and 391 s, respectively. (The spectra were recorded with 514.5 nm Ar^+ laser excitation at 20 mW.)

substituted —C=N—Ag group. By contrast, no strong band appears near 500 cm^{-1} in the spectrum of the quinoxaline sample with added Cl^- ion. The reason for this will be discussed below. The ν_{CN} band and the bending mode of the substituted —C=N—Ag group suggest that either a N=N or a N=C bond breaks during the irradiation of the adsorbate. On breaking one of these bonds the molecule becomes an ortho-disubstituted benzene-like moiety. The appearance of substituted-benzene vibrations implies that the remaining benzene ring is unbroken under our irradiation conditions. Moreover, very little fragmentation down to carbon appears to take place. (The characteristic broad carbon bands near 1400 cm^{-1} are absent.) By contrast, a broad feature in the 1400 cm^{-1} region does appear on irradiating adsorbed cinnoline even after a relatively short exposure time.

The photochemistry of phthalazine adsorbed on colloidal silver was previously reported.⁸ Its photoreaction was ascribed to a process in which the N=N bond of the molecule breaks to form an adsorbed species resembling an ortho-disubstituted benzene. The photochemistry of quinazoline adsorbed on colloidal silver was found to be somewhat more complex than that of phthalazine in that the nature of the photoreaction appears to be affected both by the surface concentration of the adsorbate and also by the coadsorption of Cl^- . At relatively high overall quinazoline concentration a strong CH SERS band is observed at 3070 cm^{-1} , and no photochemistry seems to take place (Figure 2). Only the baseline is slightly shifted downward upon irradiation. The appearance of aromatic CH stretching vibrations in the SERS spectra of aromatics suggests that the molecule is adsorbed such that the ring is oriented perpendicular to, or significantly tilted with respect to, the surface.¹⁸ We, therefore, conclude that at high surface concentrations quinazoline adsorbs

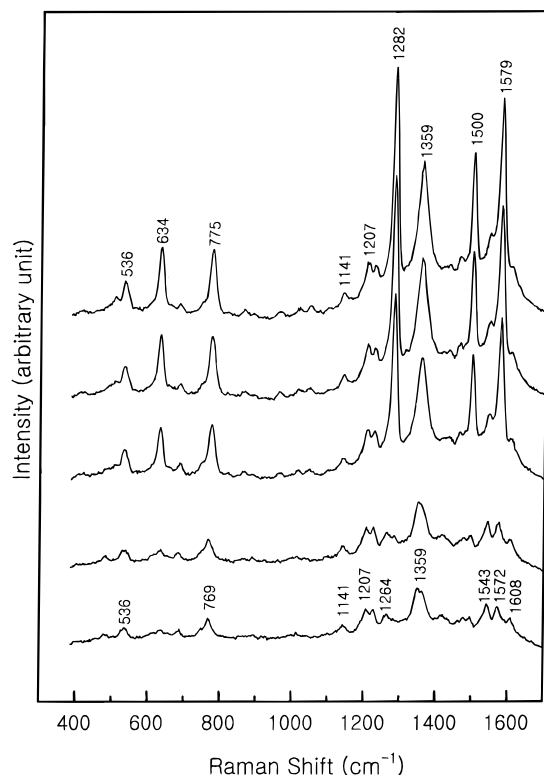


Figure 5. As in Figure 4 but with added Cl^- ion whose overall concentration was 2.8×10^{-4} M. (The spectra were recorded with 476.5 nm Ar^+ laser excitation.)

“standing up” on the surface. Under these conditions no surface photochemistry appears to take place. At relatively low overall quinazoline concentrations rapid surface photochemistry is observed; and at the same time, the CH stretching band at 3070 cm^{-1} is found to be very weak, implying that the molecule is lying flat on the surface.

The coadsorption of Cl^- ion also seems to have a directing effect on the adsorbate's orientation that offsets the effect of surface concentration. With the addition of chloride, the CH stretching band in the SERS spectrum of quinazoline is observed to be very weak even at relatively high adsorbate concentration in the solution, yet photochemistry is observed (Figure 3). This suggests that the coadsorption of Cl^- ion causes quinazoline to adopt a flat surface geometry regardless of concentration. (In speaking about concentration we are speaking of the surface concentration of the adsorbate. Although we never measure the surface concentration directly, there clearly exists an isotherm that relates, monotonically, the surface coverage to the overall concentration of the adsorbate in the colloid solution. Hence, one can speak qualitatively of greater or lesser surface concentration based on the overall adsorbate content of the solution, assuming all other parameters are held constant.) The effect of the chloride may either be an exclusionary effect, i.e., the chloride ions merely exclude the aromatic from a significant portion of the surface, or it may be a more subtle effect such as a local change in the electronic structure of the surface that causes the aromatic to prefer a π -bond even at high surface coverages.

The surface photochemistry of adsorbed quinazoline is more complex still: the relative intensities and time evolution of a number of its SERS bands were found to vary from sample to sample. This is likely due to the fact that several photoproducts form when adsorbed quinazoline is irradiated, and their relative abundances depend critically on the colloid sample.

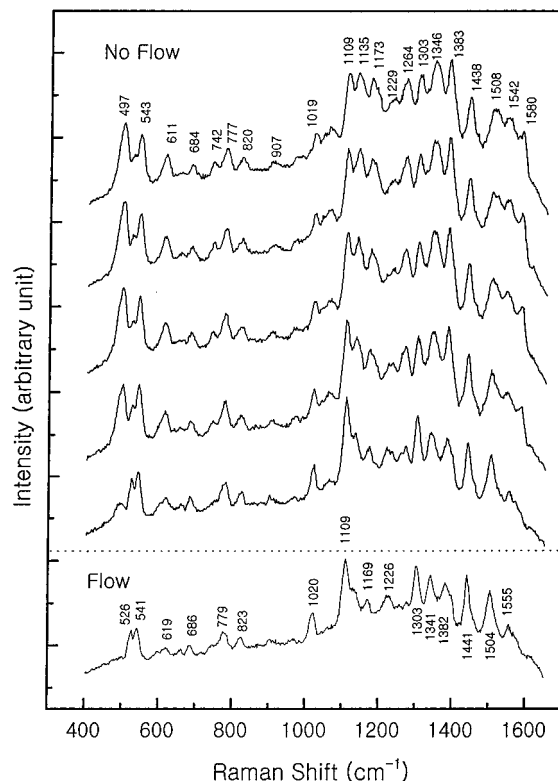


Figure 6. SERS spectra of cinnoline adsorbed on silver colloid, excited with 514.5 nm Ar^+ laser light at 20 mW. The bottom spectrum was recorded with fast flow. The upper series of spectra were collected sequentially every 1 s without flow and with the sample colloid solution contained in a capillary continuously irradiated by the laser beam. The spectra shown are (bottom to top) the 1st, 5th, 10th, and 50th spectra.

TABLE 1: Spectral Data for Photoproducts of Diazanaphthalenes

phthalazine	cinnoline	quinazoline	quinoxaline		assignment of photoproducts ^a
			no Cl^- ion	with Cl^- ion	
489 m	497 s	507 vs	505 vs		$\delta\text{-C}=\text{N}-\text{Ag}$
545 w	543 m			536 m	ν_{6a}
		552 w	564 w		ν_{6b}
		611 m	605 s		ν_{16a}
				634 s	ν_1
754 m	742 w	745 s	727		ν_4
		785 w		775 s	ν_{11}
			1070 w		ν_1
	1135				
	1173				
		1205 s	1201 s		ν_{13}
1241 s		1251 m			ν_{7a}
	1264 s		1265 s		ν_3
1278 w		1281 s		1282 vs	ν_3
1332 m	1346 s	1359 s	1350 vs	1359 s	ν_{CN}
1432 vw					
1465 s		1479 s	1494 w	1500 s	ν_{19b}
1547 s	1542 w	1539 m			ν_{8a}
		1560 vw			ν_{8a}
		1604 w	1572 s	1579 vs	ν_{8b}
1595 w	1580 w				

^a Assignment of photoproducts (ortho-benzenes) referred from ref 17.

The SERS spectra of quinoxaline samples recorded after very short laser irradiation times prepared with and without the addition of Cl^- were almost identical regardless of the laser excitation line used. The spectra were also unchanged regardless of the order of addition of chloride (from HCl or KCl) and the adsorbate to the silver sol. All of this implies that the surface geometry of adsorbed quinoxaline is not affected by presence

of Cl^- ion on the surface. Moreover, no distinct initial or evolving ν_{CH} bands were observed; only a weak shoulder at 3062 cm^{-1} on the broad water band was detected. This implies that quinoxaline and its photoproducts are adsorbed with the benzene ring flat or only slightly tilted with respect to the local surface. Although the mode of adsorption of the quinoxaline was unaffected by the presence of Cl^- , its photochemistry was greatly chloride dependent (Figures 4 and 5).

Adsorbed cinnoline underwent much slower surface photochemistry than any of the other diazanaphthalenes studied; so much so that the photochemistry had to be observed as a function of laser irradiation time in a static sample, i.e., without flow. The bottom spectrum in Figure 6 shows a strong CH stretching band near 3050 cm^{-1} . Hence the diazanaphthalene ring of cinnoline is likely oriented perpendicular to, or substantially tilted with respect to, the surface, bonding through the lone pairs of the nitrogens. Not only is the reaction rate slow with this adsorbate but the extent of reaction is also relatively slight compared to what occurs with the other diazanaphthalenes judging from the relatively small decrease in the intensities of the reagent bands even after prolonged laser irradiation (Figure 6).

Several conclusions may be drawn from the above discussion. First, when using visible illumination, the surface photochemistry of diazanaphthalenes adsorbed on colloidal silver results in the breaking of the heterocyclic benzene ring while the other benzene ring appears to remain intact. For phthalazine, it is the $\text{N}=\text{N}$ bond that is broken.⁸ Cinnoline also possesses a $\text{N}=\text{N}$ bond, and we propose that this is the bond that breaks in the surface photochemistry of this molecule. In the other diazanaphthalenes considered here, the photoreactions appear to involve the cleavage of $\text{C}-\text{N}$ bonds. No $\text{C}-\text{C}$ bonds appear to be broken.

In quinoxaline the two nitrogen atoms (at positions 1 and 4) are symmetrically equivalent. Likewise, the N_1-C_9 and the N_4-C_{10} are equivalent as are N_1-C_2 and N_4-C_3 bonds. Restricting the photoprocess to $\text{C}-\text{N}$ bond cleavage, a total of five photoproducts can be envisioned resulting from the cleavage of one or both of its $\text{C}-\text{N}$ bonds. The photoprocesses we observed could be accounted for by assuming that two photoreactions dominate (although, of course, we cannot state with confidence that others do not occur). Quinazoline possesses four distinct $\text{C}-\text{N}$ bonds and at least eight possible photoproducts resulting from the cleavage of one or two of its $\text{C}-\text{N}$ bonds. Here again, the results imply the formation of, at least, two photoproducts of which one appears to dominate.

Suggestions for the dominant photoproducts resulting from the surface-enhanced photochemistry of the diazanaphthalenes studied are shown in Figure 7. Other photoproducts might also form. Our choices were made on the basis of the following pieces of evidence. The strong band near 500 cm^{-1} was assigned to a bending mode of the $-\text{C}=\text{N}-\text{Ag}$ substituent. This band is absent in the SERS spectra of quinoxaline prepared with added Cl^- (Figure 5); hence we propose the dominant photoproduct to be the one formed when both N_1-C_2 and N_4-C_3 are broken. Another useful marker is the CN stretching vibration. This band occurs near 1332 cm^{-1} for molecules in which the N is not directly bonded to the benzene ring (as in the photoproduct resulting from phthalazine). Its frequency is higher when the nitrogen is bonded to the phenyl ring.

The SERS spectrum of the photoproduct of quinoxaline obtained in the presence of Cl^- shows only a CN stretching band at 1359 cm^{-1} ; hence we conclude that that species possesses no CN containing substituents. (One should note, in

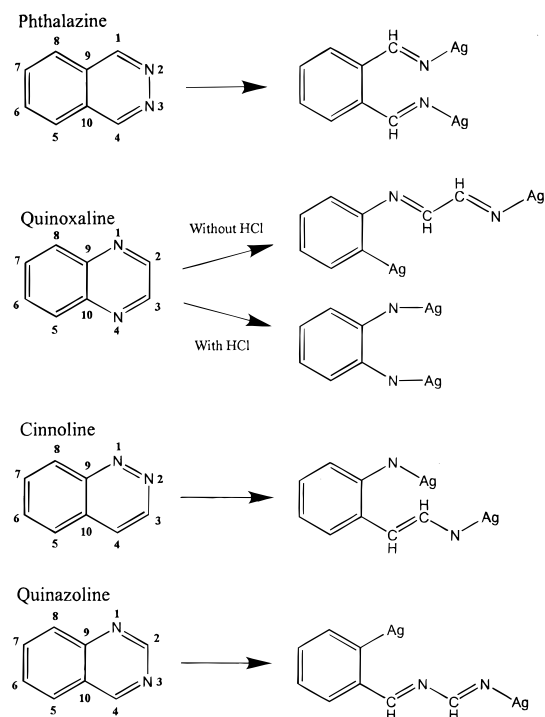


Figure 7. Proposed structures for some of the photoproducts resulting from the photodecomposition of the four diazanaphthalenes discussed in this paper adsorbed on colloidal silver.

passing, that the proposed photoproduct should potentially also have resulted in the production of acetylene. That this species is not observed in the SERS spectrum is not worrisome since acetylene would likely not compete effectively as an adsorbate with its coproduct.) The proposed photoproduct of cinnoline contains two different types of N atoms: one directly bonded to the benzene ring, the other part of the CN substituent. This is consistent with the broad CN stretching band observed at 1346 cm^{-1} (Figure 6) with components encompassing the range 1332 to 1359 cm^{-1} . (A significant contributor to that band is unreacted cinnoline which has a band at 1346 cm^{-1} .)

The wavelength dependence of the rate of photoreaction for quinoxaline is given in Figure 8 where the ratio of two photoproduct band intensities (after laser irradiation for 343 s) normalized to the intensity of the reagent band at 536 cm^{-1} is plotted as a function of the irradiation wavelength. For samples made without added Cl^- , only a single photoproduct is observed whose rate of production increases toward the blue. The spectrum of this photoproduct (referred to as **1**) is characterized by a strong band at 505 cm^{-1} . (The slight rate decrease with 457.9 nm irradiation may not be statistically significant. This slight decrease was not observed in all runs.)

With samples containing added Cl^- , two photoproducts were observed, one of which appears to be the same as that obtained in the absence of chloride, but the intensity of that species is low compared to the second. Although the SERS spectrum of photoproduct **1** appears essentially identical in the samples with and without added chloride, the wavelength dependence of its rate of formation differs according to the presence or absence of added chloride. Specifically, in the presence of chloride (Figure 8) the extent of formation of **1** decreases markedly on going toward the blue in contrast to what was observed in the absence of chloride. The other photoproduct, whose SERS spectrum is characterized by a strong band at 1282 cm^{-1} , is produced exclusively with added chloride. Its production is dominant at short wavelengths and drops to zero for wavelengths longer than $\sim 510\text{ nm}$. At the shortest wavelengths used, the

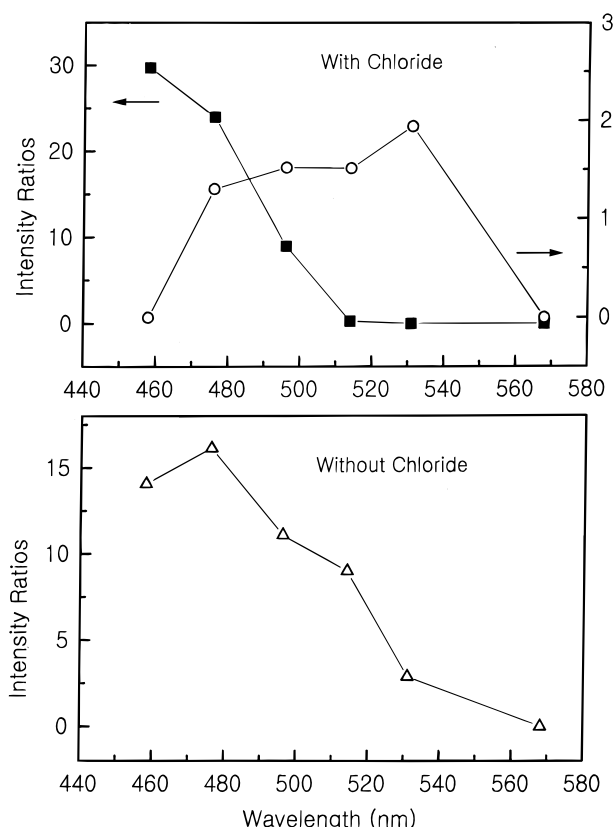


Figure 8. Intensity ratios of the photoproduct bands at 505, 1282, and 1572 cm^{-1} (corresponding to circles, squares, and triangles in figures, respectively) resulting from the irradiation of quinoxaline for 343 s normalized to the reagent band at 536 cm^{-1} as a function of irradiation wavelength. The bottom set shows results for samples containing no added Cl^- ion, the top for samples with added Cl^- ion. The circles in the upper panel refer to photoproduct **1** which appears to be identical to the sole product formed in the absence of chloride (lower panel).

product/reagent ratio for this photoproduct can reach values ~ 30 . Because it is *intensity* rather than concentration ratios that are presented in Figure 8, it is difficult to separate out the differing enhancement ratios of the product and the reagent from their surface concentration values. (Although the surface enhancement is mainly an electrochemical effect that is only slightly sensitive to the nature of the chemistry between the adsorbed reagent or product and the surface, the possibility also exists for a molecule-specific resonant effect that could affect the observed ratios by factors of the order of the 30 or so observed.)

Hence the differing wavelength dependences observed for the two photoproducts formed on irradiating quinoxaline may reflect the differing absorption spectrum and hence the different photochemical rates of two populations of reagents on the surface or the different spectrum of the enhancement factors of the two photoproducts, or a combination of both. Some reagent remains on the surface even after prolonged irradiation. Moreover, the decrease in intensity in the reagent peaks is less than the increase in intensity of the photoproduct peaks (at the shortest wavelengths), implying that the enhancement factor of the latter exceeds that of the former. The molecules studied here do not absorb in the visible; however, the wavelength dependence of the measured photochemical rate constants suggests an absorption in or near the visible.

Previously we proposed⁸ that surface photochemistry might take place through a metal-to-adsorbate charge transfer process. The incomplete reactivity observed with most of the molecules

studied suggests a number of possibilities. The model for the development of a charge transfer state for adsorbed molecules includes the broadening of the excited state of the adsorbate due to the formation of an excited state band. In a truly periodic two-dimensional assembly of adsorbate the Bloch states describing the band would encompass all of the molecules, and hence the excitation of any of those Bloch states might result in photodecomposition of any of the molecules. As photodecomposition proceeds, reagent molecules are removed from the assembly and the band structure is altered, thereby altering the reactivity of the remaining molecules. For our samples the situation is complicated further by the fact that the colloidal particles are small and their surfaces heterogeneous; hence, the assumption of a single band of Bloch states is a poor one. More likely, the system consists of a number of "clusters" of interacting adsorbate molecules on the surface, each characterized by a narrow band of states. Hence, one might achieve resonance with some of these "clusters" and not others.

Still other possibilities arise from the fractal nature of the colloidal clusters comprising our systems. It was shown¹⁹ that when fractal colloidal clusters are resonantly illuminated, the field structure at their surface is characterized by a number of "hot spots" where the field strength is very high while on most of the colloid surface the field strength is low. This implies that for a given wavelength only the molecules on a small portion of the colloid surface will react. It is also at those hot spots where the enhancement will be sufficiently high for SERS to be observed; however, at the edges of the hot spots there might be sufficient enhancement to observe, but insufficient intensity to transform the adsorbate molecules into products. Finally, as the photochemistry proceeds, the character of the colloid might change slightly, thereby changing the location of the hot spots bringing a fresh crop of molecules into the high-field region. (The possibility that the adsorbed molecules or their photoproducts are mobile on the surface taking them in and out of high-field regions must also be considered.)

These considerations must also be borne in mind in considering the effect of added chloride.

Previously we alluded to two possible roles for the adsorbed chloride in affecting the surface photoreactivity of the coadsorbed molecules: the exclusion of the molecules from surface sites and the modification of the electronic properties of the underlying silver. The data presented in Figure 8 cannot conclusively eliminate either of these, but it does favor the explanation in terms of the modification of electronic structure of the silver. Hence, with and without chloride one still forms photoproduct **1** as indicated by its SERS spectrum but the wavelength dependence of its formation changes as a result of the coaddition of chloride. (One might still argue, however, that photoproduct **1** forms at two different sites, one of which is blocked by the chloride, and that the "missing" portion of the reactivity at short wavelengths is due to the removal of the population from the surface which possesses an absorption band in the vicinity of that wavelength. While we cannot reject such an explanation outright, there is an element of coincidence about it that renders it less likely.) More likely, the chloride affects the band structure of the surface so as to modify the branching ratio for the formation of the two photoproducts so that in the absence of chloride only **1** forms; while with added chloride two products form, the one characterized by the vibration band at 1282 cm^{-1} being dominant. If one subscribes to this explanation, the differing appearance intensities with wavelength reflect the modification of the surface electronic structure.

Strong qualitative evidence was presented showing the effect

of adsorbate orientation and the coadsorption of chloride on its surface photochemistry. For example, quinazoline π -bonded to the surface shows significant photoreactivity, while σ -bonded quinazoline showed essentially no photoreactivity. Likewise, the presence or absence of coadsorbed chloride was shown to modify the spectral sensitivity of the photoprocesses. Both of these effects, together with the fact that the (one-photon) photochemistry took place with visible light for colorless molecules, suggest the evolution of new adsorbate/surface resonances likely associated with metal-to-molecule charge transfer. The orientational sensitivity of the molecule's photochemistry is then due to the differing resonances formed with the molecules bonded to the surface in the two manners discussed. (A polarization effect, i.e., the alignment of the molecular transition dipole with the local surface normal along which the local electric field strength is larger, also comes to mind. However, the suppression of the tangential component of the electric field at the blue end of the laser wavelengths used is very poor; hence we reject this possibility.)

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