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Adsorbate Photochemistry on a Colloid Surface: Phthalazine on Silver

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Phthalazine adsorbed on colloidal silver surfaces is found to convert photochemically to a product in which the N═N bond of the molecule likely breaks to form an adsorbed species resembling an ortho-substituted benzene. The photochemical kinetics was studied using a simple flow cell. The photochemical rate constant was found to be large in the visible region of the spectrum, increasing toward the blue. We show, incidentally, that SERS spectra of phthalazine reported previously by us and by others were heavily contaminated by the spectral features of the photoproduct. Hence previous explanations of the unusual excitation wavelength and coverage dependence are incorrect. The photochemical reaction is found to be a one-photon process; hence, the large absorption cross section in the visible is likely due to a metal to molecule charge transfer transition. (Solution-phase phthalazine is transparent in the visible.) It is likely that a significant number of published SERS spectra of other molecules contain spectral features due to photoproducts. By using dynamic methods such as that described, one can avoid these complications.

Introduction

Enhanced surface photochemistry of molecules adsorbed on surfaces capable of producing surface-enhanced Raman spectra has been proposed theoretically and observed experimentally.[1−5] The photochemical rate is increased by the same field enhancement mechanism responsible for surface-enhanced Raman scattering (SERS)[6] which draws its strength from the dipolar emissions accompanying localized surface plasmon (LSP) excitations in very small particles composed of metals that have particularly strong LSP absorptions. It is now known that the most intense surface-enhanced effects occur in assemblies of highly interacting small metal particles[7] such as the large fractal clusters of colloidal metal particles formed after an adsorbate is added to the metal colloid solution.[8] This fact can lead to potential complications in the kinetics of the enhanced photochemistry of molecules adsorbed on metal colloid clusters as a result of the possible involvements of thermal or photofragmentation of the colloid cluster assemblies[9] or the photoassisted aggregation of colloids. Photoaggregation may be due either to the increase in the van der Waals *C*-factor resulting from the expansion of the particle's polarizability upon excitation[10] or to the reduction in the net charge on the colloid particle's surface following photochemistry, which in turn leads to a reduction in the potential barrier to aggregation. The diffusion or convection of reagent- or product-bearing colloidal particles into and out of the illuminated area of the colloid may complicate the kinetics further. The diffusion rate may, in turn, be affected by the photofragmentation of the colloidal clusters or by the energy release accompanying photochemistry so that the diffusion rates of the reagent-bearing and product-bearing colloid clusters may differ. The importance of diffusion and convection will depend on the geometry of the cell in which the photochemistry is carried out and on the size of the illumination source, which in the case of a tightly focused laser beam could be rather small, thereby increasing the importance of the role of diffusion or convection.

In the present study we report on the enhanced photochemistry of phthalazine adsorbed on silver colloid aggregates. The kinetics was studied using a simple flow method that allows fresh, reagent-bearing colloid to be exposed to a laser beam for continually increasing lengths of time. The use of flow cells in Raman spectroscopy is not new.[11] Its specific application to the study of the photochemical reactivity of adsorbate on aqueous colloid by SERS has also been reported previously.[12]

We also show, incidentally, that our earlier interpretation of the wavelength dependence of the SERS spectra of phthalazine[13] in terms of the surface selection rules for SERS was wrong. What we, in fact, observed was a series of SERS spectra consisting of varying mixtures of adsorbed phthalazine and a photoproduct resulting from its surface-enhanced photochemistry at a rate that was wavelength dependent. (We do not imply that the theory of the surface selection rules of SERS is wrong, merely that because of its tendency to photoreact, phthalazine is a poor choice of adsorbate to illustrate SERS selection rules.)

Surface photochemistry also appears to have complicated the interpretation of the SERS spectra of phthalazine reported by other groups. Takahashi's group, for example, investigated the SERS spectrum of phthalazine adsorbed on Ag electrode surfaces as a function of electrode potential, solution concentration,[14] and the coadsorption of various anions.[15] Their SERS spectra were found to depend on all of these variables as well as on the excitation wavelength. These observations were interpreted in terms of the orientation of the adsorbate, which presumably depends on its concentration in solution and on the specific adsorption of anions, while the excitation wavelength dependence was interpreted in terms of resonance enhancement by a charge-transfer band. The SERS spectrum of phthalazine was also reported from a system consisting of a 60 Å SiO_2 film sputtered over a 50 Å silver island film.[16] The spectra were similar to those observed with colloids.[13]

Although in the present study we report in detail the surface photochemistry of a single system, we have performed preliminary experiments on a variety of molecules, and we suspect that many SERS spectra reported in the literature are contaminated with the spectral features of the products of surface photochemistry. Often the photoproduct is structurally related

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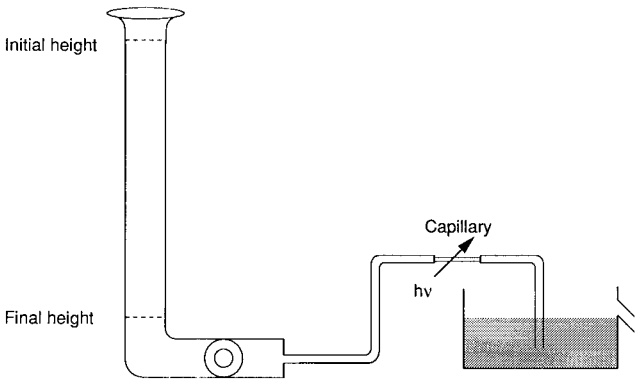

Figure 1. Schematic of the flow cell.

to its parent molecule; hence, the spectroscopic features observed might be interpretable, with little difficulty, in terms of vibrational modes of the original adsorbate. The degree of contamination will depend on experimental details such as the size and shape of the spectroscopic cell used and the size of the exciting laser beam since in many cases what is observed is the steady state distribution resulting from the competition between the photochemical rate and the rate at which fresh colloid is brought into the laser beam by diffusion. Hence a great deal of the photoproduct will be observed either when the photochemical rate is high or when the diffusion rate is low. In a previous study, for example,[9] when the colloid sample was contained in a cuvette whose size was very much greater than the diameter of the laser beam, the SERS spectrum observed was essentially only that of the reagent. In contrast, when the sample was irradiated in a capillary whose size was comparable to that of the laser beam and hence where the flow of fresh reagent into the laser beam was less efficient, the SERS spectrum became dominated by the photoproduct within a few seconds. The mode of detection is also critical. Current multichannel techniques require considerably less exposure time than the more traditional single-wavelength detection used with scanning spectrometers. It may, accordingly, be essential to re-examine a great deal of the older SERS literature to ensure that interpretation was not based on spectral features belonging to the photoproducts.

Experimental Section

Silver sols were prepared as described previously.[17] 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. Phthalazine was introduced into the colloid as an aqueous solution. The overall concentrations of phthalazine in the three sample solutions used were 2.7×10^{-5}, 2.7×10^{-3}, and 2.7×10^{-7} M. Most of the studies were carried out with the 2.7×10^{-5} M sample. Raman spectra were recorded approximately 5 h after the colloid/adsorbate samples were prepared.

Poly(vinylpyrrolidone) (pvp, MW 40000) 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 0.027% by weight. Experiments were also carried out in the absence of pvp to ascertain that the polymer did not noticeably affect the spectroscopy or the kinetics.

The flow cell is shown schematically in Figure 1. It 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, to maintain the final level constant. The outlet tube emptied the colloid under the surface of the water in the basin to minimize turbulence. Colloid samples were used only once to avoid contamination by the photoproduct.

Surface-enhanced Raman spectra were excited by a focused Ar ion or Kr ion laser (Lexel Model 3000 and Model 3500, respectively) traversing the capillary. SERS spectra were recorded using a Spex 1887C Triplemate spectrometer equipped with a multichannel charge-coupled device (CCD) detector. One hundred and fifty or 200 spectra were collected in sequence in each flow experiment. The accumulation time for each spectrum was 5 s. The time evolution of the SERS bands was obtained by constructing a matrix whose columns constituted the 150 spectra and whose rows comprised the time evolution of each point in the spectra. The Raman spectrum of CCl_4 was used as both a wavenumber and power calibration when changing the laser excitation wavelength. UV−visible spectra were recorded using a Varian Cary 3 UV−visible spectrometer.

Flow Kinetics

In determining the photochemical kinetics of phthalazine adsorbed on silver colloid, we made use of the fact that the flow rate though a capillary fed from a continuously emptying reservoir decreases exponentially with time.[19] (The same method can be applied to the study of any photodynamical processes involving colloid aggregates such as the fragmentation.) To introduce the important variables of the technique, let us first consider an idealized situation in which the glass capillary has a square cross section illuminated with a laser beam of uniform intensity with a square cross section of side L. We also assume that the intensity attenuation of the laser beam through the photoreagent solution is negligible and that the reaction is a simple conversion of reagent, A, to product, B, in a first-order, irreversible, reaction initiated by the absorption of n photons. (Departures from the ideal situation will be discussed below.) The photoreagent begins to be exposed to the laser when it first crosses into the illuminated section of the capillary, and it continues to be irradiated until it crosses out of the illuminated portion.

Because the flow rate is a function of time, the exposure time, t_{ex}, which is equal to the width of the laser beam times the cross-sectional area of the capillary divided by the flow rate (volume/time), will also be a function of time. Since the concentration of photoreagents and products will be determined from the SERS signal excited by the same laser that produces the photochemistry, the SERS signal will be an appropriate average of the Raman signal over the illuminated portion of the capillary.

The concentration of the reagent, A, after exposure to the laser for a time t_{ex} is given by

$$A = A_0 \exp(-k_1 t_{ex})$$

where A_0 is the initial concentration of A. (The fact that the concentration of species A will be written as A should not cause confusion.) 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 concentration of product B can be determined from the relation $B = A_0 - A$.

The instantaneous height, h, of the reagent head will depend on time according to the expression

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

where h_0 is the initial height. The flow rate in units of volume/second is given by $-A_{gc}\, dh/dt$. Hence the exposure time for a particle that has travelled a distance z in the laser beam will be given by

$$t_{ex} = [A_c z \tau_0/(A_{gc} h_0)] \exp(t/\tau_0)$$

where A_c and A_{gc} are, respectively, the cross-sectional areas of the capillary and the cylindrical reagent reservoir, and τ_0 is a constant proportional to $A_{gc}/(\rho g)$, where ρ is the aqueous colloid density and g, the gravitational acceleration.

We will assume that the flow is in the z-direction, the exciting laser travels in the y-direction, and the Raman signal is collected in the x-direction. The Raman intensity of a band belonging to the photoreagent or the photoproduct will be proportional to their average concentrations in the illuminated portion of the capillary, which is given by

$$\bar{A} = (1/L)\int_0^L A\, dz$$

This results in the expression

$$\bar{A} = \frac{A_0}{qk_1L}[1 - \exp(-qk_1L)] \tag{1}$$

and

$$\bar{B} = A_0 + \frac{A_0}{qk_1L}[\exp(-qk_1L) - 1] \tag{1'}$$

where

$$q = [A_c\tau_0/(A_{gc}h_0)] \exp(t/\tau_0) \tag{2}$$

The Raman intensity associated with a photoproduct band will therefore have the form

$$I_{Raman} = I\sigma_B B + b_B \tag{3}$$

(with an analogous form for a reagent band), where σ_B is the (band-specific) Raman cross section, I is the laser intensity, and b_B is a base-line function.

If the rate of diffusion or convection of reagent-bearing and/or product-bearing colloid is comparable to the rate of the photoreaction, then the effect of these processes must be included in the analysis. In particular, when the rate of influx of reagent-bearing colloid into the illuminated region is equal to the rate of eflux of product-bearing colloid out of it (a not unreasonable assumption), then the rate equations will resemble those describing a reversible reaction in which product returns to reagent with a rate constant k_{-1}. In that case the equation analogous to (1) becomes

$$\bar{A} = \frac{A_0}{(k_1 + k_{-1})qL}\left\{\frac{k_1}{k_1 + k_{-1}}[1 - \exp(-(k_1 + k_{-1})qL)] + k_{-1}qL\right\} \tag{4}$$

where q is defined in (2). (The same equation will be valid when the photoproduct can, in fact, thermally revert to the reagent.) The corresponding expression for the average product concentration is once again given by

$$\bar{B} = A_0 - \bar{A}$$

These expressions can be related to the Raman intensity using (3).

A more realistic analysis of the problem would take the following points into account: (1) The laser beam does not have a uniform intensity distribution. (The argon or krypton ion lasers that we use have a nearly Gaussian beam profile.) (2) The capillary has a round cross section so that the distance traversed by a ray of infinitesimal cross section constituting the laser beam is a function of the position along the diameter of the capillary, and the capillary will, in general, truncate the laser beam. (3) The liquid is transported by Poiseuille flow, which has a parabolic velocity distribution across the diameter of the capillary; hence the exposure time is not uniform across the capillary. (4) The colloidal solution is colored, resulting in the attenuation of the intensity of the laser beam as it crosses the capillary and of the Raman-scattered light traversing some portion of the solution.

Under these circumstances the average concentration of the photoreagent detected by the Raman signal would be determined from the expression

$$\bar{A} = \frac{A_0}{4r_0^2L_z}\int_{-r_0}^{r_0} dx \int_0^{l(x)} dy \int_0^{L_z} dz\, I(x,y,z) \exp(-aI^n(x,y,z)\, t'_{ex}) \tag{5}$$

where r_0 is the diameter of the capillary, $l(x)$ is the cross section of the capillary at x traversed by the laser beam, which is given by $l(x) = 2(r_0^2 - x^2)^{1/2}$. $I(x,y,z) = I_0(x,z) \exp(-\beta y)$, β being the attenuation coefficient through the colloid at the wavelength of the laser. (An equivalent term for the attenuation of the Raman-scattered light at the Raman-shifted frequency can also be included.) $I_0(x,z)$ is the intensity profile of the laser beam incident on the capillary. L_z is the length of the capillary exposed to the laser and

$$t'_{ex} = \frac{L_z}{\nu_0(1 - r^2/r_0^2)} \exp(t/\tau_0) \tag{6}$$

where $r = (x^2 + y^2)^{1/2}$. The integration in (5) must be carried out in the order z, y, x.

It may, at first sight, seem improper for the entire length of the capillary, L_z, to appear in (6) rather than the "illuminated portion" of the colloid as before. If, however, the laser beam is taken to have a Gaussian profile, then its extent will be infinite, but its effect will be truncated in the z-direction by the length of the capillary and in the x-direction by its width. Of course, the predominant photochemical effect of the laser beam will be concentrated in a small region on the order of 4 standard deviations of the Gaussian profile.

The experimental setup is such that the laser beam is tightly focused to a spot smaller than the inner diameter of the capillary. Additionally, the collection optics for the Raman are enlarging so that only the central portion of the image of the laser beam traversing the capillary is passed by the slits into the spectrograph. Hence, the denominator in (6) can be written as $\nu_0(1 - y^2/r_0^2)$ since the laser beam has, effectively, negligible width in the x-direction and $l(x)$ can, therefore, be replaced by the constant $2r_0$. The truncation of the laser beam image also suggests that in carrying out integration (5) using (6), the denominator of (6) may be expanded in orders of y^2/r_0^2 and only first-order terms (second order in y) retained. The very small size of the capillary also allows the attenuation of the

laser beam and the Raman-scattered light to be ignored. The Gaussian beam profile does not allow an analytic solution of (5). However, replacing the Gaussian by a uniform intensity distribution effectively assumes an average over intensity which would affect the absolute values of the rate constants determined by fitting the experimentally measured kinetics data to (5) but should not affect their relative values, at least not for single-photon processes. For multiple-photon processes ignoring the Gaussian profile could result in more significant error. Fortunately, we will show below that the photoreaction reported here is a one-photon process. Moreover, all of the arguments presented here will be in terms of the relative rather than the absolute values of the rate constants so that the above-mentioned averaging will not be significant.

One concession made to the fact that the Gaussian profile of the laser beam was ignored was to allow the parameter τ_0 to be adjustable even though its value can be (and was) independently determined by measuring the rate of flow through the capillary. In fact the value of τ_0 returned by the fitting program was always larger by approximately a factor of 1.8 than the independently determined value of τ_0. And although values of k_1 can be determined from the fitting parameters since the factors in the pre-exponential term of q (eq 2) are known and a value of L was estimated, it should be borne in mind that k_1 always appears in the product qk_1L so that the uncertainty in the value of τ_0, which occurs in the expression for q, and in the value taken for L, which is an estimate of the width of the Gaussian profile of the laser beam, will affect the value of k_1 (in addition to other sources of uncertainty). Values for k_1 are quoted in the discussion simply to indicate the general range in which they fall.

The y-dependence of t'_{ex}, was dealt with in one of two ways: (i) integral 5, with all of the above-mentioned simplications was numerically integrated over y, (ii) an analytic expression was determined for (5) by assuming the aforementioned expansion in terms of y^2/r_0^2. In the latter case the approximate expression

$$\bar{A} = \frac{2A_0}{3qk_1L}[1 - (1 - qk_1L/2)\exp(-qk_1L)] \qquad (7)$$

was determined as a replacement for eq 1. The analogous expression for (1′) is obtainable as before. Fitting the experimental kinetic data either to eq 7 or to the numerical integral of (5) produced values of the rate constants which differed only a little from those obtained by fitting to eqs 1 and 1′. The relative values of the rate constants determined from the two sets of equations were even less significantly different. Likewise, fitting eqs 1 and 1′ or eq 4 and its counterpart for B to the experimental data produced equally good fits. Hence, we could not determine on the basis of the goodness of fit alone whether the reaction is reversible or not. We did, however, ascertain that with our reaction cell parameters the reaction rate is very much greater than either the rate of diffusion and/or convection or any thermally induced back reaction. Accordingly, on the basis of these findings and for the sake of ease of discussion we will present our data in terms of eqs 1 and 1′ while keeping in mind the approximations made.

Results and Discussion

A representative series of SERS spectra of phthalazine adsorbed on colloidal silver recorded during flow are shown in Figures 2−4. Spectra excited with 476.5, 514.5, and 568.2 nm Ar or Kr ion laser lines are shown in the figures. Measurements were also made with 457.9, 496.5, and 530.9 nm excitation. For most runs 150 spectra were collected sequentially every 5 s. The spectra reported in Figures 2−4 are (bottom to top) the 2nd, 30th, 60th, 90th, 120th, and 150th spectra corresponding to a mean time: 7.5, 147.5, 297.5, 447.5, 597.5, and 747.5 s after the flow was initiated. In Figures 2−4 the base line is displaced in equal intervals for clarity. The background signals did not increase substantially with time.

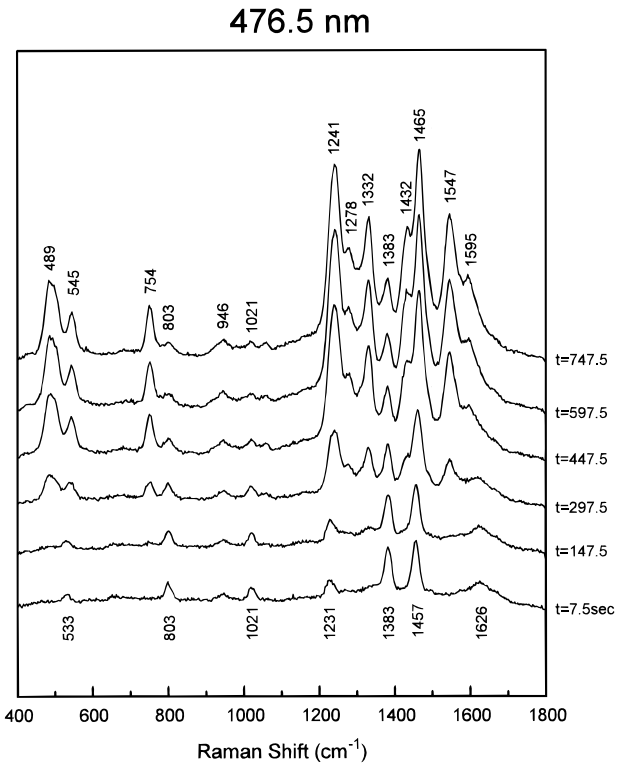

Figure 2. The 2nd, 30th, 60th, 90th, 120th, and 150th SERS spectra (bottom to top) of phthalazine adsorbed on silver colloid of a 150 spectrum series recorded using multichannel detection and the flow cell shown in Figure 1 (476.5 nm Ar^+ laser excitation and 20 mW).

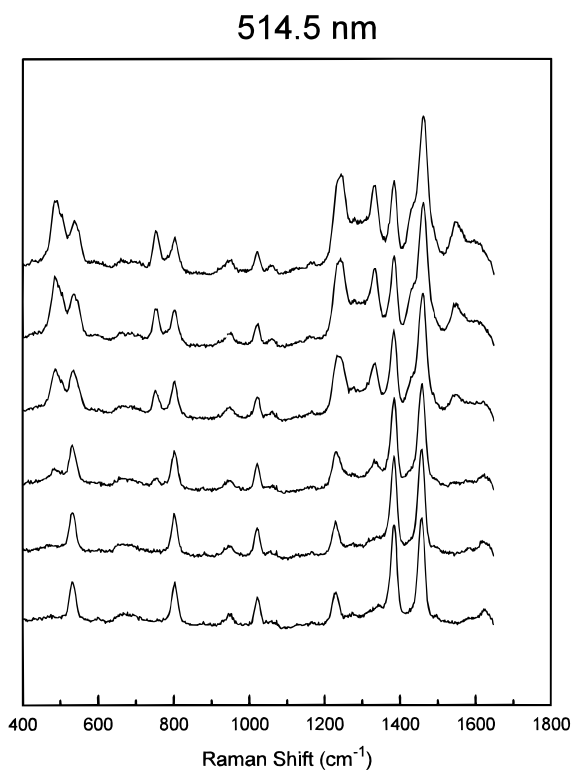

Figure 3. Same as in Figure 2 but with 20 mW of 514.5 nm Ar^+ laser excitation.

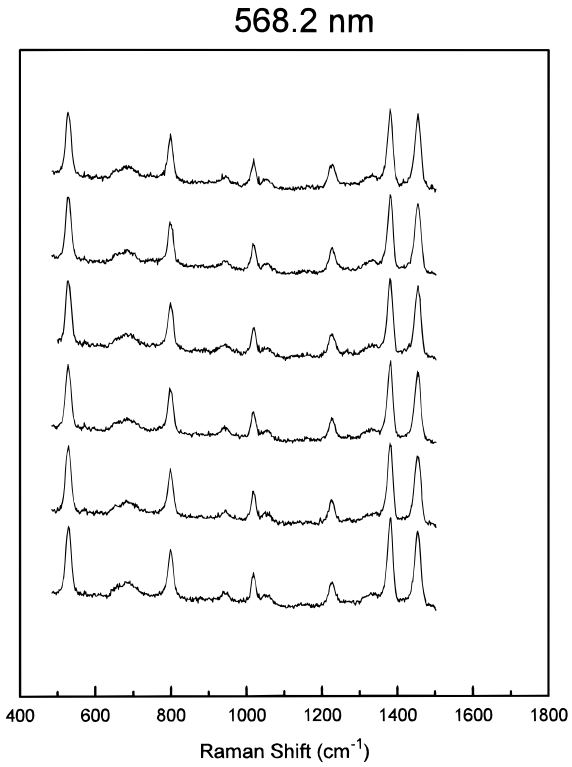

Figure 4. Same as in Figure 2 but with 20 mW of 568.2 nm Kr^+ laser excitation.

A molecule in the sample was exposed to the laser for an exponentially increasing time interval equal to a maximum exposure time of 9.7×10^{-5} s when the first spectrum was collected to a maximum exposure time of 0.33 s for the 150th spectrum. These estimates assume a laser spot size of 10 μm and $\tau_0 = 91.5$ s. When 200 spectra were recorded, the maximum irradiation time during the collection of the 200th spectrum was 5.1 s.

The bottom spectrum in each figure, corresponding to the 2nd spectrum of the series of 150 spectra, is rather simple and almost identical regardless of the excitation wavelength. It is, moreover, very similar to that published previously[13] for phthalazine contained in a 1 cm cuvette excited with 602 nm R6G dye laser light. All of the strong bands in this spectrum are assignable to a_1 modes of phthalazine. Excitation with 568.2 nm Kr ion laser radiation (Figure 4) produces almost no change in the SERS spectrum with irradiation time, even when prolonged irradiation was used. On the other hand, excitation with shorter laser wavelengths results in the appearance of several new bands with increasing exposure time. The new bands clearly result from the irradiation since they are absent when very short exposure times were used. Moreover, the intensities of the initial bands of a_1 symmetry decrease with increasing exposure time while the new bands increase, suggesting that these new bands are due to a photoproduct resulting from a photoreaction of phthalazine.

The spectra containing the new bands are similar to the previously published[13] SERS spectrum of phthalazine excited with 514.5 or 488 nm Ar ion laser light. In that and other publications[14] the new SERS bands were assigned to b_1 and b_2 modes of phthalazine. Coincidentally, the frequencies of the new bands are close to those of normal modes of phthalazine,[18] allowing the error in interpretation to pass without undue suspicion.

Although the identity of the photoproduct cannot be determined with certainty, the frequencies of the new bands correspond closely to those of ortho-substituted benzene such as *o*-diethylbenzene.[20] A possible interpretation is that the N=N bond of phthalazine is broken during the photoprocess with the newly freed N ends forming two Ag−N bonds. Because the frequencies of the Ag−N oscillators are different from those of the C−N, C−C, and C−H groups, the resulting surface complex would behave vibrationally like an ortho-substituted benzene. We see evidence of only a single photoproduct or, rather, of only a single photochemical step, as opposed to sequential steps. In particular there is little evidence that the product photoreacts further to form graphitic carbon[9,21] with bands near 1400 cm^{-1}, as is often seen with other adsorbates.

The suggested structure of the photoproduct implies that the vibrational signature of the benzene ring should dominate the new bands. This is in fact what is seen. (See, for example, the top spectrum of Figure 2.) The frequency of the strongest band at 1465 cm^{-1} is close to the ν_{19a} band of *o*-xylene[20] at 1468 cm^{-1}, while the rapidly growing bands at 489, 545, 754, 1241, 1278, 1332, 1432, 1465, 1547, and 1595 cm^{-1} can be, respectively, assigned to ν6b, 6a, 11, 7a, 3, 14, 19a, 19b, 8a, and 8b vibrational modes of ortho-substituted benzenes.[20]

Although the time evolution of all of the bands was recorded and considered, the discussion will focus on the kinetics of growth of the band at 754 cm^{-1}, assigned to the ν_{11} mode, which is well separated from other, potentially interfering, bands.

The rate at which the new bands increase with laser exposure time is greater than the rate at which the bands of phthalazine decrease. This is presumably a reflection of the relative Raman (or more accurately SERS) cross sections of the two species. The greater apparent SERS cross section of the photoproduct is in keeping with the frequent observation that the SERS intensity of strongly chemisorbed species is greater than that of weakly adsorbed species. The possibility that the phthalazine molecule and its photoproduct may adopt different surface geometries would also contribute to the differing SERS cross sections. There is evidence in the SERS spectra to suggest that phthalazine stands up on the silver, i.e. that it bonds to the surface through the lone pairs on the nitrogen atoms so that its C_2 axis is substantially perpendicular to the local surface. Likewise, the absence of a strong ν_1 band of benzene among the photoproduct bands suggests that its benzene ring is significantly inclined with respect to the local surface.[22] This mode of bonding is not difficult to reconcile with the suggestion that the N=N bond is broken in the photoproduct. If so, then the two N−C bonds become double bonds, leaving a lone pair and a single electron on each of the nitrogens, each of which would form a single bond with a silver atom of the silver surface. The distance between the (now unbonded) nitrogens would also be appropriate for bonding to two adjacent silver atoms. The disposition of the bonds and the lone pairs on the nitrogens would make the inclined geometry the preferred one.

Figure 5 shows the time evolution of the SERS intensity of the photoproduct band at 754 cm^{-1} observed when the colloid is irradiated with 514.5 nm Ar ion laser light. The four traces represent differing laser intensities. The jagged lines are experimental data, and the smooth lines are recalculated curves after fitting to eq 3 using eq 1′. The best fit was obtained with $a = 12.6$ s^{-1} mW^{-1} and $n = 0.85$, where these constants refer to the rate constant, $k_1 = al^n$. The four curves in Figure 5 were fit simultaneously using common values of the parameters but independent values for the base lines. The value of a was calculated by assuming $A_{gc}/A_c = 91$, $h_0 = 10$ cm, and $L = 10$ μm. The value of $\tau_0 = 91.5$ s was returned by the fit. Acceptable fits were obtained with n in the range 0.85−1.15. The experimental data could not be fit with n equal to or in the vicinity of 2. We conclude that phthalazine undergoes a

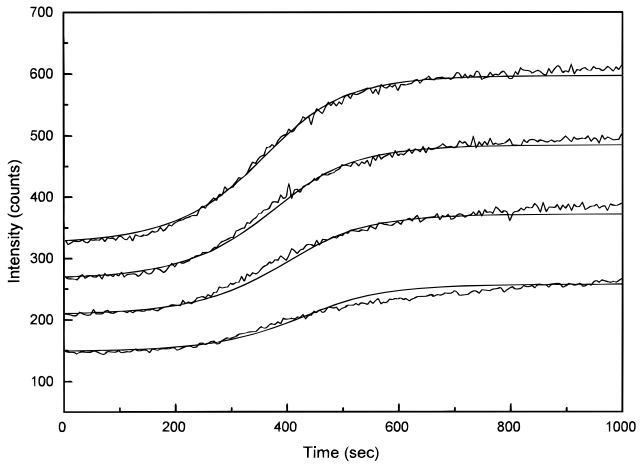

Figure 5. Time evolution of the SERS intensity of the 754 cm^{-1} band excited with 514.5 nm Ar^+ laser light. Jagged lines are experimental data. Smooth lines are fitted curves. The laser power used was (top to bottom) 50, 40, 30, and 20 mW.

photochemical process on the Ag colloid surface that is initiated by a one-photon process. Additionally, the rate is relatively fast among the handful of reactions of this sort investigated to date.

The photochemical rate constant is found to be wavelength dependent in the visible region. The time evolution of the SERS band intensity at 754 cm^{-1} is shown in Figure 6 for six excitation wavelengths. The rate of photoproduct formation, which is almost zero with 568 nm Kr ion laser irradiation, increases rapidly on going toward the blue. With 20 mW laser power, the values of the rate constant k_1 obtained by fitting eqs 3 and 1′ to the data shown in Figure 6 are found to be 0, 115.8, 143.8, 180.5, 291.7, and 295.9 s^{-1} for 568.2, 530.9, 514.5, 496.5, 476.5, and 457.9 nm Ar or Kr ion laser irradiation, respectively (assuming the parameters listed above). The rate constants are plotted in Figure 7 as a function of excitation wavelength.

Parenthetically, if diffusion or convection makes the photoreaction appear reversible (or if it is actually thermally reversible), then continuous wave irradiation (without flow) would result, after a time, in a steady state with steady state concentrations of species A and B given by

$$A_{ss} = \frac{k_{-1}A_0}{aI + k_{-1}} \tag{8}$$

and

$$B_{ss} = \frac{A_0 aI}{aI + k_{-1}} \tag{8'}$$

The steady state concentration of B would be both laser-intensity dependent and also wavelength dependent through $a(\lambda)$. This may explain the previously reported excitation wavelength dependence of the SERS spectra of phthalazine[13] which were recorded using a scanning spectrometer and with the same contained in a cuvette, making the role of convection or diffusion more pronounced and allowing sufficient time for the establishment of a steady state. (Alternatively or additionally, the previously observed wavelength dependence[13] may be due to inhomogeneous broadening of the absorption band responsible for the photochemistry. With yellow light only a portion of the adsorbed phthalazine molecules are affected, while with blue light a much larger portion photoreacts.) An experiment was performed to determine the relative rates of the photoreaction and diffusion, convection, or any reverse reaction. With the

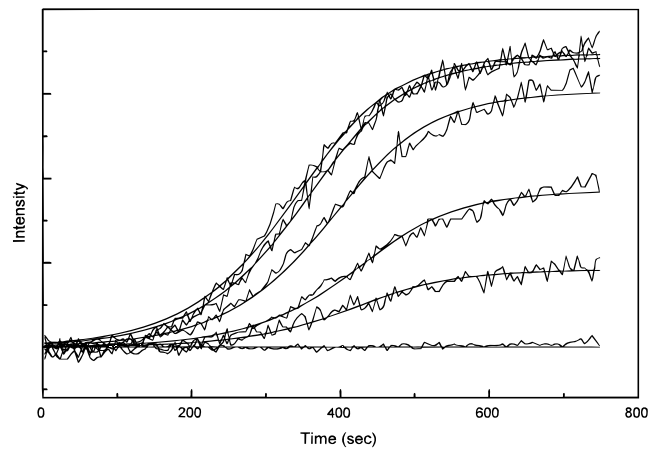

Figure 6. Time evolution of the SERS intensity of the 754 cm^{-1} line excited with several Ar and Kr laser wavelengths. The laser power was 20 mW in all cases. Intensities were calibrated against the Raman spectrum of CCl_4, and the base lines were removed. The wavelengths used were (top to bottom) 476.5, 457.9, 496.5, 514.5, 530.9, and 568.2 nm.

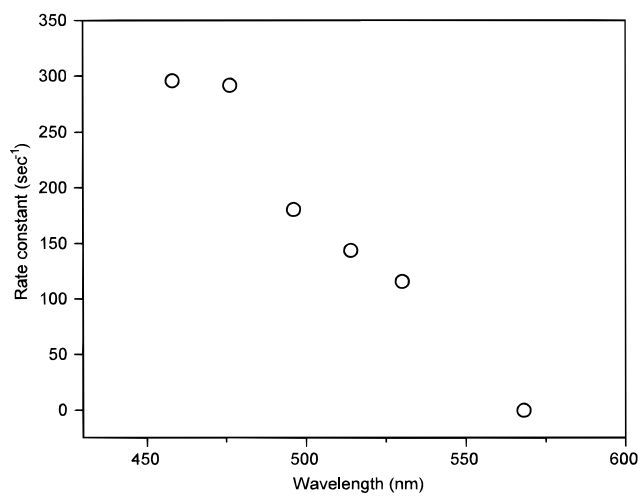

Figure 7. Plot of the photochemical rate constant derived from the data shown in Figure 6 as a function of excitation wavelength.

sample contained in a 1.8 mm capillary and without flow the sample was exposed to the laser through a variable speed chopper that blocked out the beam for a duration 11 times longer than the irradiation time. The SERS spectrum was then followed as a function of time, and the experiment was repeated as a function of chopper speed. Our analysis of the results suggests that the photochemical reaction of phthalazine on silver does not appear to be reversible, nor is the rate of diffusion or convection competitive with the photochemical rate.

The wavelength dependence of the rate constant k_1 shown in Figure 7 suggests that the photoreaction which converts phthalazine to its photoproduct is initiated by a one-photon process in the visible with a threshold at approximately 570 nm and reaches a maximum in the blue (although the limited range of our lasers prevented us from determining the position of the maximum with certainty). Gas- or solution-phase phthalazine has no absorptions in the visible region. Colloidal aggregates do have localized surface plasmon (LSP) absorptions in the region of the specturm indicated in Figure 7; however, if the process were one involving the excitation of LSP modes of the colloidal aggregates followed by energy transfer to low-lying states of the molecule, then several visible photons would be required to excite the molecule. This would presumably be indicated in the dependence of the rate constant upon the laser intensity (barring saturation). There is no evidence for this sort

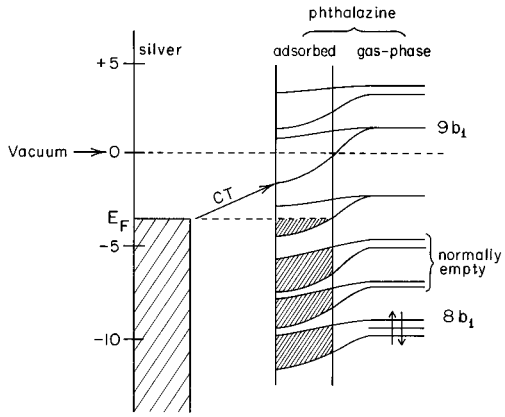

Figure 8. Proposed charge transfer scheme to explain the wavelength dependence of the photochemical rate constant shown in Figure 7.

of process, although saturation cannot be utterly excluded. There is, however, the possibility that the wavelength dependence of k_1 is due to a metal to molecule charge-transfer transition, as illustrated in Figure 8. The ionization potential of phthalazine is reported[23] to be approximately 9.2 eV. Although there is no report of the energy positions of excited states of phthalazine above the HOMO and below the vacuum level, inverse photoemission measurements on naphthalene[24] indicate the presence of a number of states in that energy range.

If phthalazine is strongly adsorbed on silver, whose work function is approximately 4.2 eV, then the vacuum level of the adsorbate would be pinned to that of the silver, and all states lying between the HOMO of the molecule and the Fermi energy of the metal could be filled by charge transfer. This would result in the formation of an anionic adsorbed species. The electronic structure of the adsorbate would be described by two-dimensional Bloch states, and hence the molecular levels of the adsorbed molecules would broaden into bands. The charge on the adsorbate due to the metal to molecule charge transfer (CT) would result in an energy stabilization of the states of the adsorbate (so-called relaxation stabilization) which, classically, comes about as a result of the interaction of the charged adsorbate with its charge-conjugate image. This is shown schematically in Figure 8.

The absorption suggested by the spectrum of k_1 in Figure 7 might then occur from the Fermi level of the metal to an excited state of the adsorbate. A good candidate for this adsorbate excited state would be one which lies in the vicinity of the vacuum level in the gas phase and would, therefore, be stabilized to a position below the vacuum level in the adsorbed molecule so that the metal to molecule charge-transfer absorption would lie in the visible. (One should distinguish between the static CT which occurs upon adsorption and the dynamic CT accompanying a photon-induced electronic transition.)

Quantum-mechanical excited state calculates for phthalazine were not found. Accordingly, we simply illustrate this process with an extended Hückel calculation performed using the program Hyperchem. The HOMO is found to be a b_1 orbital situated at −12.07 eV below vacuum (cf. the experimental ionization potential of 9.2 eV). There are actually rather few orbitals found to lie near or just above the vacuum level. The best contender is a b_1 orbital predicted to come at 0.88 eV in the gas phase. Populating this orbital would result in $^{1,3}A_1$ excited states in the neutral phthalazine or a $^2B_1$ state in the singly charged phthalazine anion. A stabilization on the order of 2 eV upon adsorption so as to bring the CT absorption into the visible is quite reasonable.[24] Actually, one need not postulate the formation of a significantly anionic species capable of large-scale relaxation stabilization *prior* to the photon-induced

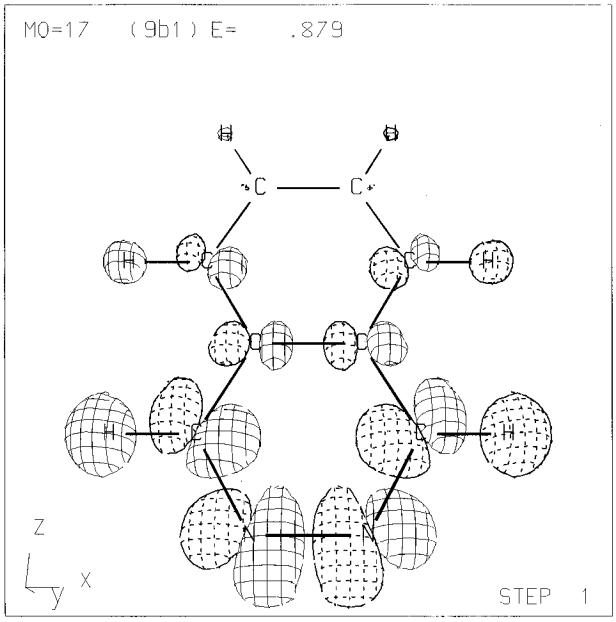

Figure 9. Representation of an orbital possibly implicated in the N═N bond scission proposed to result from the photochemistry of phthalazine adsorbed on silver.

electronic excitation of the phthalazine for this argument to operate. The CT accompanying photoexcitation may be sufficient to bring about this stabilization.

The occurrence of extensive charge transfer and the adsorption process could, and most likely would, result in serious reordering of the orbitals in the phthalazine-derived adsorbed species. This fact, coupled with the overall crudeness of the calculation, suggests that one should not place much credence in the assignment of the excited state. Nevertheless, it is interesting to note that the excited b_1 orbital identified above is one which is highly localized on the N═N bond and is strongly antibonding (Figure 9) so that populating this state in gas-phase phthalazine would result in the reduction of the bond linking the nitrogens to a single bond. When the molecule is adsorbed on silver, the weakening of the N═N bond may be sufficient to break it completely since by doing so, two Ag−N bonds may be formed. There may also be additional weakening of the N═N bond due to the formation of an anionic adsorbate. (In the gas phase, exciting a neutral molecule by the absorption of a photon would, in general, leave the molecule neutral. In contrast, on a metal surface, metal to molecule CT can simultaneously excite and charge the molecule.)

Finally one should note that although the wavelength dependence of k_1 seems to maximize (or, at least, cease to grow rapidly) in the blue, the CT absorption band associated with it would continue to increase sharply into the UV region of the spectrum. This is because the wavelength dependence of k_1 depends both on the spectrum of the absorption cross section (a) and on the wavelength-dependent intensity associated with the enhanced local field. The field enhancement increases toward the red, the region where silver colloid clusters absorb. This behavior has been reported previously and checked once again in this study (Figure 10) by noting the trend in the intensity of the strong phthalazine band at 1383 cm^{-1} as a function of excitation wavelength. CCl_4 was used as an 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 10 is a measure of the true, relative enhancement. By using data from early (i.e., very short exposure time) spectra in the kinetic runs, the relative wavelength dependence of the SERS enhancement

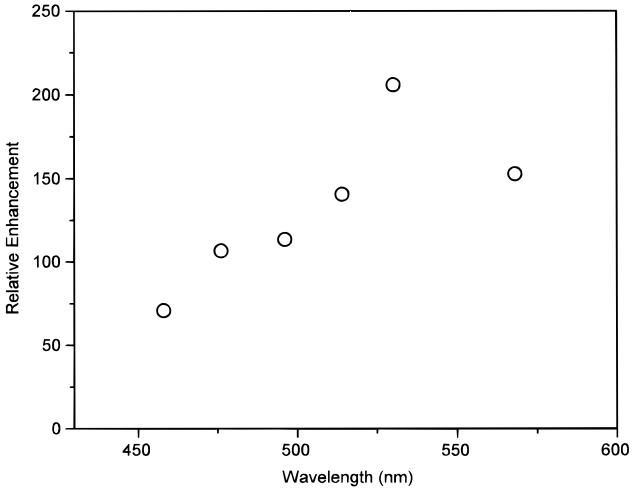

Figure 10. Measured wavelength dependence of the SERS enhancement of phthalazine adsorbed on colloidal silver.

of phthalazine can be obtained without danger of complication from the photochemistry.

The possible role of colloid particle aggregation or cluster fragmentation[9] in the kinetics was also investigated. Since aggregation or fragmentation is known to affect the UV−visible spectrum of the colloid in the LSP region, we measured the absorption spectrum of a series of adsorbate-bearing colloid solutions while they were being irradiated with a high-power laser beam defocused so as to illuminate all of the sample solution. No significant change in the absorption spectrum was observed. Aggregation or fragmentation was, therefore, excluded as a major contributor to the observed kinetics.

The effect of adsorbate coverage was also investigated by preparing two samples with 2.7×10^{-7} and 2.7×10^{-3} M overall phthalazine concentration, very different from the one used in the above experiments. Since there is an isotherm that connects the surface coverage of adsorbate to its overall concentration in solution, the three samples should correspond to significantly different surface coverages of phthalazine. For the low-concentration sample, the time evolution followed a pattern similar to those shown in Figure 3 but with a much lower rate of product production. Even with 50 mW of 514.5 nm laser light, the photoproduct bands in the 150th were weak. The slow growth may reflect a number of contributions. In addition to the trivial consequence of the lower surface coverage, the low adsorbate concentration may also result in only limited aggregation of the colloid, and it is in the aggregates that the most intense electromagnetic fields occur.

With the high (2.7×10^{-3} M) phthalazine concentration samples, the observed rate of reaction was very rapid so that photoproduct bands were already visible in the first few spectra of the 150 spectrum series; however, the intensity of the photoproduct bands saturated rapidly, achieving something resembling a steady state, well before the 150th spectrum was reached. (With 514.5 nm excitation the final spectra approximately resembled spectrum 60.) Additionally, a broad background signal centered at approximately 1400 cm^{-1}, often associated with graphitic carbon, appeared in some spectra. The growth of graphitic carbon was not observed with the 2.7×10^{-5} M phthalazine samples, whose photochemical behavior is reported in Figures 2−4. This observation implies that both the rate of product formation and the final product/phthalazine ratio depend on initial coverage.

The more rapid rate of product formation with increased coverage is expected. The incomplete conversion of phthalazine to its photoproduct when the initial coverage is high, although unusual, may be due to the fact that for high coverage the silver surface cannot sustain the level of charge transfer needed to excite all of the adsorbate. Additionally, if our interpretation is correct that phthalazine binds to the surface standing up while its photoproduct binds in a more horizontal orientation, then at full coverage one can pack more reagent molecules than product molecules on the surface. At or near full coverage it would, therefore, be impossible to convert the photoreagent to the photoproduct completely.

The observations of Takahashi et al.[14,15] parallel those reported in this article as regards both laser excitation wavelength and concentration. Although those authors interpreted their results in terms of the surface reorientation of phthalazine, it is clear that they were in fact observing photochemistry. The long irradiation times they required to record their spectra with a scanning spectrometer facilitated the photochemistry.

Conclusions

(i) A flow cell was used to record the SERS spectrum of molecules adsorbed on aggregated silver colloid clusters and simultaneously to initiate photochemistry in the adsorbate. Adsorbed phthalazine was found to undergo facile photochemistry to a photoproduct in which the N═N bond is likely broken, allowing the two N atoms to bind strongly to the silver surface. (ii) The previously reported SERS spectra of phthalazine both by ourselves and by other groups and especially the unusual excitation wavelength dependence of these spectra were shown to be due to photochemistry rather than to wavelength-dependent normal and tangential electric field components[13] (the so-called surface selection rules) or to the reorientation of the adsorbed phthalazine.[14,15] (iii) The photochemical rate constant was found to be proportional to laser intensity, suggesting that the photochemistry is initiated by the absorption of a single photon. (iv) The wavelength dependence of the measured photochemical rate constant with its large value in the visible is best understood in terms of a metal to molecule charge-transfer process. (v) It is likely that a number of previously reported SERS spectra of other molecules are, in fact, those of photoproducts or of mixtures of the molecules initially introduced into the colloid together with their photoproducts. Several of these systems should be reinvestigated using dynamical techniques such as the one described here in order to reduce the likelihood of improper assignment.

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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) Leung, P. T.; George, T. F. *J. Chem. Phys.* **1980**, *85*, 4729.
(4) Wolkow, R. A.; Moskovits, M. *J. Chem. Phys.* **1987**, *87*, 5858.
(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) Stockman, M. I.; Shalaev, V. M.; Moskovits, M.; Botet, R.; George, T. F. *Phys. Rev. B* **1992**, *46*, 2821.

(8) Weitz, D. A.; Oliveria, M. *Phys. Rev. Lett.* **1984**, *52*, 1433.

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

(10) Kreibig, U.; Eckstein, H. *Z. Phys. D* **1993**, *26*, 239.

(11) Keifer, W.; Bernstein, J. *Appl. Spectrosc.* **1971**, *25*, 500. Woodruff, W. H.; Spiro, T. G. *Appl. Spectrosc.* **1974**, *28*, 74.

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

(13) Moskovits, M.; Suh, J. S. *J. Phys. Chem.* **1984**, *88*, 5526.

(14) Takahashi, M.; Fujita, M.; Ito, M. *Chem. Phys. Lett.* **1984**, *109*, 122.

(15) Takahashi, M.; Furukawa, H.; Fujita, M.; Ito, M. *J. Phys. Chem.* **1987**, *91*, 5940.

(16) Walls, D. J.; Bohn, P. W. *J. Phys. Chem.* **1990**, *94*, 2039.

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

(18) Mitchell, R. W.; Glass, R. W.; Merritt, J. A. *J. Mol. Spectrosc.* **1970**, *36*, 310.

(19) *Mechanics*; Symon, K. R., Ed.; Addison-Wesley: Massachusetts, 1971.

(20) *Assignments for Vibrational Spectra of Seven Hundred Benzene Derivatives*; Varsanyi, G., Ed.; John Wiley & Sons: New York, 1974; and references therein.

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

(22) Moskovits, M.; Suh, J. S. *J. Phys. Chem.* **1988**, *92*, 6327.

(23) Dewar, M. J. S.; Worley, S. D. *J. Chem. Phys.* **1969**, *51*, 263.

(24) Frank, K. H.; Yannoulis, P.; Dubbe, R.; Koch, E. E. *J. Chem. Phys.* **1988**, *89*, 7569.

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