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LETTERS

Effect of Surface Roughness on the Photodissociation Threshold of Chlorobenzene and 3-Chloropyridine Adsorbed on Silver

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We have investigated the photodissociation of chlorobenzene and 3-chloropyridine adsorbed on smooth and rough Ag surfaces. Photolysis of adsorbed chlorobenzene and 3-chloropyridine with UV radiation results in C–Cl bond dissociation. Biphenyl and bipyridyl desorb from the surface near 400 K, and AgCl desorbs near 800 K in postirradiation temperature-programmed desorption. Compared to a smooth surface, there is a red shift in the photodissociation threshold for both molecules when adsorbed on a rough surface. Possible mechanisms for the red shift are discussed. This study demonstrates the importance of substrate morphology on surface photochemistry.

Introduction

There has been much interest in recent years in the photochemistry of molecules adsorbed on solid surfaces.[1-3] These studies have been stimulated by an interest in understanding and exploiting enhanced optical processes at surfaces with applications in laser-assisted chemical vapor deposition, semiconductor device fabrication, and the development of optical sensors.[4]

On metal surfaces, substrate-mediated processes play an important role in surface photochemistry.[1-3,5-15] Excitation mechanisms involving electron transfer from the substrate to the adsorbate have been shown to cause a significant red shift in the photodissociation threshold when molecules are adsorbed on single crystal metal surfaces.[1-3,8-15]

The effect of surface morphology, in particular surface roughness, on substrate-mediated photochemistry or through direct excitation of the adsorbate has not been as well characterized. The discovery of surface-enhanced Raman scattering (SERS) and the importance of surface morphology in SERS[16] have prompted theoretical studies concerning the role of surface roughness in photochemistry.[17-19] Nitzan and Brus have modeled the rough surface as isolated microscopic spheres protruding from the surface.[17] Their calculations predict an enhancement in the photochemical yield due to an increase in the molecular absorption cross section on a rough surface. The enhancement factor, defined as the absorption cross section of the adsorbed molecule relative to the free molecule, was calculated to be approximately 10-100, several orders of magnitude smaller than for SERS cross sections. There have been some reports in the literature of enhanced absorption on Ag films.[20,21]

In a more recent study, Das et al. also predicted an enhancement in the photodissociation cross section for molecules adsorbed on a rough surface.[19] In their calculations, the rough surface was modeled as a hemispherical protrusion on a semiinfinite flat plane, and the effects of radiative and nonradiative quenching were taken into account. The enhancement factor was found to depend on particle size and shape and the molecule–surface distance.

There have been very few experimental studies on the photochemistry of molecules adsorbed on rough metal surfaces. Using a focused CW Ar ion laser, Goncher et al. monitored the growth of surface graphite as a function of laser power and wavelength for a series of aromatics at and near a rough silver surface.[22] An enhanced two-photon process was proposed for the photodecomposition of benzene, pyridine, pyrazine, aniline, and acetophenone at 406.7 nm. Similar studies by Wolkow and

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Moskovitz have also shown enhanced multiphoton photochemistry on rough silver surfaces.[23] In comparison, other experiments found the rate of photochemical degradation of rhodamine 6G was greatly reduced on a rough silver surface.[24]

In related experiments on metal particles, Suh et al. determined that a two-photon process initiated the decomposition of 2-pyrazinecarboxylic acid adsorbed on colloidal silver.[25] A CW Ar ion laser was used for photolysis and as a probe through SERS to measure the growth of graphitic carbon as a function of laser power and wavelength. Chen and Osgood examined the photodecomposition of dimethylcadmium adsorbed on cadmium particles with 257-nm photons by monitoring the growth of the Cd particles. They found evidence for structured particle growth which was related to the electric field intensity around the particle.[26]

The various factors that lead to an increase or decrease in photochemical yields will be dependent on molecule–surface interactions. For instance, the enhanced absorption for molecules near a surface will compete with increased rates of energy transfer. In particular, enhanced absorption may be expected for a molecule adsorbed on a rough surface or metal particle while quenching is also enhanced.[18,19] The relative rates of these different processes—excitation, quenching, and, therefore, reaction—will be a function of surface morphology.

We have initiated a study of the UV photodissociation of molecules adsorbed on smooth and rough Ag surfaces.[27] The smooth surface, an atomically flat Ag(111) surfaces, is prepared by standard polishing techniques while the rough surface is prepared by ion sputtering the same Ag(111) surface. This method of sample preparation allows us to compare the effect of surface roughness on the same sample. Silver was chosen as a substrate because of its sharp, low plasma frequency, making it the best enhancing substrate found thus far. Rough silver surfaces are known to enhance optical processes such as SERS[16] and second harmonic generation.[28] In addition, there have been several studies reported in the literature, by White and co-workers, on the photochemistry of adsorbates on single crystal silver surfaces.[1,9-11,29]

In this Letter, we report our results on the effect of surface roughness on the photodissociation threshold of adsorbed C_6H_5Cl and C_5H_4ClN. We find, compared to the smooth surface, a red shift in the photodissociation threshold when C_6H_5Cl and C_5H_4ClN are adsorbed on a rough surface. This study demonstrates the importance of substrate morphology, in particular surface roughness, on surface photochemistry.

Experimental Section

An ultrahigh-vacuum (UHV) chamber with a typical base pressure of 2×10^{-10} Torr is used in these experiments. The chamber is equipped with a cylindrical mirror analyzer (CMA) and a quadrupole mass spectrometer (QMS). The QMS is mounted on a linear translator and can be positioned to within a few millimeters of the crystal face. A glass cone shield with a 3-mm-diameter pinhole is placed over the ionizer of the QMS so that molecules desorbing from the front face of the crystal will be preferentially detected in temperature-programmed desorption (TPD).[30] Both the Auger electron and mass spectrometers are interfaced to a 286-PC for data acquisition and analysis. Currently, five mass signals can be monitored simultaneously in TPD. The UHV chamber is also equipped with three dosers and an ion sputter gun.

The Ag crystal is mounted on a tantalum cup that can be cooled with liquid nitrogen to 120 K. The tantalum cup is resistively heated and in direct contact with the Ag crystal. The power supply used to heat the sample is interfaced to a PC, providing a linear temperature ramp from 120 to 900 K. Heating rates of 1.5 K/s are typically used for TPD. The temperature of the Ag sample is measured with a chromel–alumel thermocouple wire inserted into a small hole drilled in the front face of the crystal. The sample holder is held by a precision translation stage and a differentially pumped rotary drive.

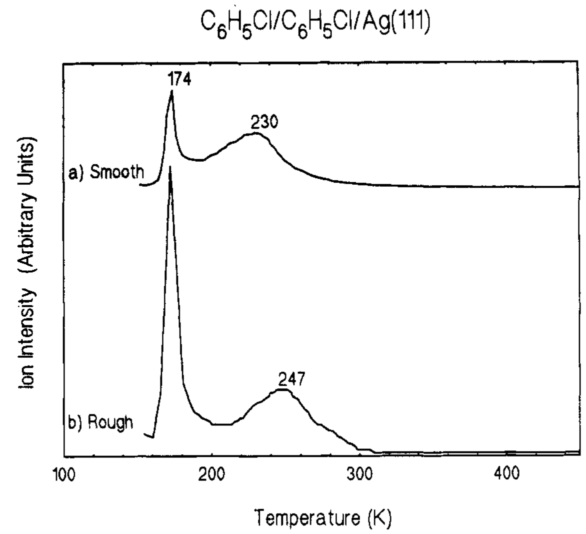

Figure 1. TPD traces for the molecular desorption of chlorobenzene (amu = 112) from Ag(111) after approximately 5-langmuir exposure: (a) smooth and (b) roughened surface.

The Ag sample is cleaned by 2-kV Ar^+ bombardment to remove sulfur and oxygen impurities from the surface. A smooth surface is prepared by annealing the sample to 900 K. A rough surface is prepared by 2-kV Ar^+ sputtering at room temperature for several hours. This procedure has been shown to give a Ag surface that exhibits SERS.[31]

C_6H_5Cl and $3\text{-}C_5H_4ClN$ were purchased from Aldrich and freeze–pump–thawed several times prior to use. Gases are introduced by back-filling the chamber, and gas exposures are given in units of langmuirs, where 1 langmuir = 1×10^{-6} Torr·s.

The third harmonic of a 10-Hz Nd:YAG laser (Continuum YG661-10) and the frequency-doubled light from a Nd:YAG pumped dye laser (Continuum TDL-60) are used to photolyze the sample at various wavelengths. The p-polarized laser beam irradiated the sample at an angle of 30° with respect to the surface normal. Photolysis times of 2 h were typical, and the laser fluence was kept below 10 mJ/cm^2 per pulse in order to minimize thermal effects. The sample temperature was maintained at 120 K during photolysis. The maximum temperature rise at the surface is calculated to be less than 15 K.[32] In addition, the sample was biased −90 V during photolysis to eliminate electron-induced chemistry from stray electrons in the vacuum chamber.

Results and Discussion

TPD of Chlorobenzene and 3-Chloropyridine from Smooth and Roughened Ag(111). Prior to photochemical studies, the surface chemistry of C_6H_5Cl and $3\text{-}C_5H_4ClN$ was characterized with TPD. In Figure 1, TPD traces are shown for the molecular desorption of C_6H_5Cl from a smooth and rough Ag surface following adsorption at 145 K. At low exposures, C_6H_5Cl desorbs from the smooth surface with a desorption rate maximum near 230 K. As the exposure is increased (>3 langmuirs), a second feature grows in at lower temperature with a desorption rate maximum of 174 K. The low-temperature feature does not saturate with increasing exposure and is therefore assigned to multilayer desorption of C_6H_5Cl. The high-temperature peak does saturate and is assigned to desorption of the monolayer. Our results are in excellent agreement with those of Zhou and White for C_6H_5Cl desorption from Ag(111); i.e., molecular desorption of chlorobenzene is quantitative on Ag(111).[29]

Also shown in Figure 1 is the molecular desorption trace of C_6H_5Cl from a roughened Ag surface. For the monolayer, the desorption rate maximum shifts to higher temperatures by 17 K at saturation coverage, whereas the temperature of the multilayer

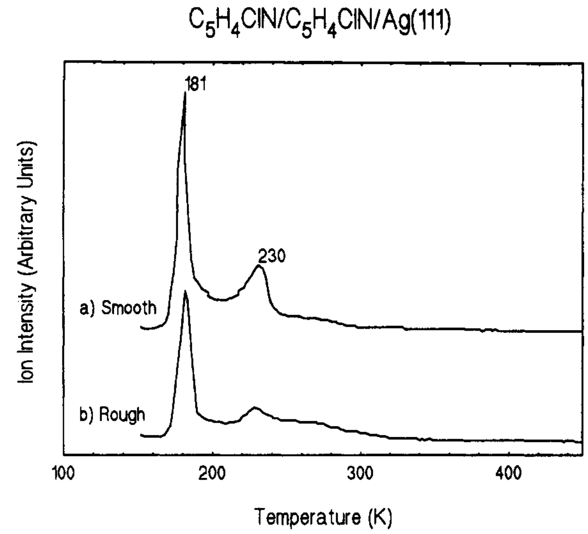

Figure 2. TPD traces for the molecular desorption of 3-chloropyridine (amu = 113) from Ag(111) after approximately 3-langmuir exposure: (a) smooth and (b) roughened surface.

desorption rate maximum remains at 174 K. The higher temperature for the desorption rate maximum of the monolayer on the rough surface suggests a stronger interaction with the surface. The increased integrated area and the breadth of the monolayer TPD peak on the roughened Ag surface reflect a larger surface area and greater degree of site heterogeneity. Other desorption products, including H_2, biphenyl, and AgCl, that may desorb from the rough surface because of an increase in surface reactivity due to the formation of defect and low coordination sites were not detected in TPD.

3-C_5H_4ClN was adsorbed on a smooth and rough Ag surface at ~145 K. On the smooth surface, there are two molecular desorption peaks with desorption rate maxima near 230 and 181 K (see Figure 2a). The high-temperature peak grows in first with increasing exposure and saturates at about 1 langmuir, whereas the low-temperature peak does not saturate with increasing exposure. Accordingly, the high-temperature peak is assigned to monolayer desorption and the low-temperature peak to multilayer desorption. No other desorption products were detected on the smooth surface. The shape of the multilayer desorption feature is the same on both the smooth and rough surfaces, but the monolayer desorption peak is more asymmetric and has a high-temperature shoulder on the rough surface (see Figure 2b). There is a small amount of H_2 desorption near 450 K from the rough surface, indicating some decomposition.[27] Other products, such as bipyridyl and AgCl, were not detected in TPD on the rough surface.

UV Photodissociation Threshold Measurements of C_6H_5Cl and 3-C_5H_4ClN Adsorbed on Smooth and Roughened Ag(111). In accordance with previous results,[29] UV photolysis of 1 ML[33] of C_6H_5Cl on the smooth surface with 280-nm photons results in the detection of two products in TPD:biphenyl ($C_{12}H_{10}$) and AgCl. Zhou and White have shown that broad-band UV photolysis of chlorobenzene on Ag(111) results in C–Cl bond cleavage.[29] Biphenyl desorbs with a desorption rate maximum near 390 K, and chlorine desorbs as silver chloride at higher temperatures with a maximum near 800 K. Similar reaction products are detected in TPD after UV photolysis of chlorobenzene on a roughened Ag(111) surface. Zhou and White proposed that adsorbed phenyl groups formed upon photolysis recombine during heating in TPD. However, it has recently been proposed that biphenyl forms directly on the surface during photolysis.[34]

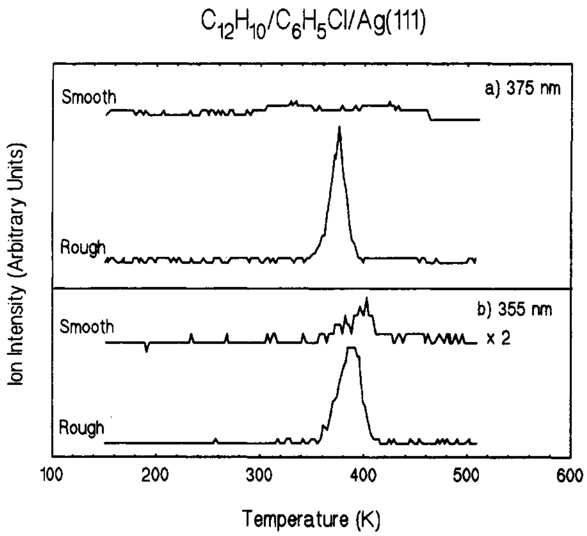

Figure 3. (a) Biphenyl (amu = 154) is detected in TPD from roughened Ag(111) but not from a smooth Ag(111) surface after excitation of adsorbed chlorobenzene with 375-nm photons. (b) Biphenyl (amu = 154) is detected in TPD from smooth and roughened Ag(111) after excitation of adsorbed chlorobenzene with 355-nm photons. Biphenyl was not detected in TPD from either surface after excitation of adsorbed chlorobenzene with 400-nm photons. Approximately 2 h of irradiation time was used, and the laser fluence was kept below 10 mJ/cm^2 per pulse.

Analogous photochemistry is observed for 3-C_5H_4ClN adsorbed on silver. Photolysis of 1 ML[35] of 3-C_5H_4ClN with 280-nm photons results in the desorption of bipyridyl, $C_{10}H_8N_2$,[36] and AgCl in TPD. The desorption rate maximum is near 410 K for bipyridyl. Therefore, UV-induced C–Cl bond dissociation results in the formation of pyridyl groups (or bipyridyl) and atomic chlorine on the surface, similar to the photoinduced chemistry of adsorbed chlorobenzene.

Although similar photoproducts are detected in TPD on both the smooth and rough surfaces, there is a difference in the wavelength dependence on the two surfaces. The photodissociation threshold is at longer wavelengths on the rough surface. Figure 3 shows the TPD trace for biphenyl desorption from Ag(111) and roughened Ag(111) after photolysis at two wavelengths, 375 and 355 nm. Biphenyl is detected in TPD after excitation of C_6H_5Cl with 375-nm photons when adsorbed on the rough surface but not on the smooth surface (Figure 3a). Excitation of C_6H_5Cl with 355-nm photons results in the formation of biphenyl on both surfaces (Figure 3b). We estimate that less than 10% of the adsorbed molecules are converted to products.

Biphenyl is not detected in TPD after photolysis with 406-nm photons on either surface.[37] Therefore, the photodissociation threshold of C_6H_5Cl lies between 406 and 375 nm on the rough surface and between 375 and 355 nm on the smooth surface. On the basis of these measurements, we can place an upper limit of 0.4 eV on the shift in the photodissociation threshold of adsorbed C_6H_5Cl due to surface morphology.

The photodissociation threshold of adsorbed 3-chloropyridine is also red-shifted on the rough surface relative to the smooth metal surface. Excitation with 355-nm photons followed by heating to ~400 K results in the desorption of bipyridyl from the rough surface but not the smooth one (see Figure 4a). Bipyridyl desorbs from both surfaces after excitation with 320-nm photons (see Figure 4b). Bipyridyl is not detected in TPD after photolysis with 375-nm photons on either a rough or smooth surface.[37] Therefore, we can place an upper limit on the shift in the photodissociation threshold of 0.6 eV for adsorbed C_5H_4ClN.

The measured photodissociation thresholds on the smooth and rough surfaces are energetically below the gas-phase UV absorption bands for either chlorobenzene or 3-chloropyridine.[38] It has been proposed by Zhou and White that the photodissociation of C_6H_5Cl adsorbed on Ag is most likely due to a substrate-mediated process, similar to that found for adsorbed CH_3Cl, but with a lower cross section.[29] The smaller cross section was attributed to a larger degree of quenching due to the greater interaction with the surface and the flat π-bonded chlorobenzene

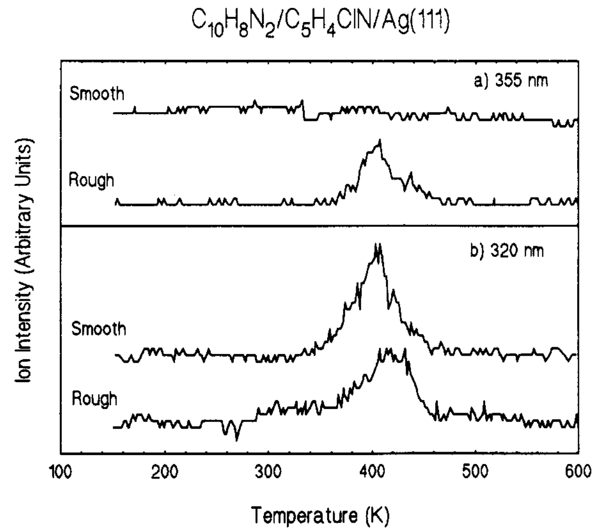

Figure 4. (a) Bipyridyl (amu = 156) is detected in TPD from roughened Ag(111) but not from a smooth Ag(111) surface after excitation of adsorbed 3-chloropyridine with 355-nm photons. (b) Bipyridyl (amu = 156) is detected in TPD from smooth and roughened Ag(111) after excitation of adsorbed 3-chloropyridine with 320-nm photons. Bipyridyl was not detected in TPD from either surface after excitation of adsorbed 3-chloropyridine with 375-nm photons. Approximately 2 h of irradiation time was used, and the laser fluence was kept below 10 mJ/cm^2 per pulse.

as compared with the tilted halogen-bonded methyl chloride. The adsorbate orientation and cross section for 3-chloropyridine are currently unknown.

There are two effects, kinetic and energetic, that may give rise to the red shift in the observed photodissociation threshold for C_6H_5Cl and C_5H_4ClN adsorbed on a rough surface. A kinetic effect would suggest that the rate of dissociation is too slow on the smooth surface at the long wavelengths used in this study and therefore, an insufficient amount of products is formed. An energetic effect would suggest that the electronic structure, in particular the local electronic structure, is the cause of the difference in thresholds on the smooth and rough surface.

The kinetic effect could arise from enhanced electromagnetic fields near surface protrusions on a rough surface. Studies by Chen et al. using second harmonic generation have determined an enhancement of 10^4 in the electric field strength due to surface roughness.[28] The enhanced electromagnetic field strength at the surface may lead to a greater number of substrate electrons and therefore an increase in the rate of photodissociation. Alternatively, there is the possibility of an enhanced molecular multiphoton absorption process on the rough surface due to the enhanced local fields. Although, multiphoton processes seem small considering that photons of longer wavelengths than the measured threshold wavelengths would also be effective in causing dissociation. Similarly, photochemistry due to photons at $2h\nu$ by second harmonic generation cannot explain the results because longer wavelengths would be effective in causing dissociation.

Another plausible explanation for the observed red shift on the rough surface may be related to the energetics and the local electronic structure. There has been some evidence that the local electronic structure is important in metal surface photochemistry. Recently, it has been proposed that the substrate-mediated process for the photodissociation of methyl bromide on Pt(111) and Cu(111) involves a localized electron transfer from the substrate d-band to the σ^* C–Br orbital.[15] Ukraintsev et al. have discussed the role of the local work function to account for the dissociation dynamics of adsorbed CH_3Br.[39] Alternatively, enhanced excitation of surface plasmon resonances on a rough surface could be related to the observed threshold shift.[40] Current studies underway in our laboratory will address possible kinetic and electronic effects to clarify the role of surface morphology on surface photochemistry.

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References and Notes

(1) Zhou, X.-L.; Zhu, X.-Y.; White, J. M. *Surf. Sci. Rep.* **1991**, *13*, 73 and references therein.

(2) Ho, W. In *Desorption Induced by Electronic Transitions*, DIET IV; Betz, G., Varga, P., Eds.; Springer-Verlag: Berlin, 1990; p 48.

(3) Polanyi, J. C.; Rieley, H. In *Dynamics of Gas-Surface Interactions*; Rettner, C. T., Ashfold, M. N. R., Eds.; Royal Society of Chemistry: London, 1991; p 329.

(4) *Laser Microfabrication, Thin Film Processes and Lithography*; Erlich, D. J., Tsao, J. Y., Eds.; Academic: Boston, 1989.

(5) Buntin, S. A.; Richter, L. J.; King, D. S.; Cavanagh, R. R. *J. Chem. Phys.* **1989**, *91*, 6429.

(6) Budde, F.; Heinz, T. F.; Loy, M. M. T.; Misewich, J. A.; de Rougemont, F.; Zacharias, H. *Phys. Rev. Lett.* **1991**, *66*, 3024.

(7) Gadzuk, J. W.; Richter, L. J.; Buntin, S. A.; King, D. S.; Cavanagh, R. R. *Surf. Sci.* **1990**, *235*, 317.

(8) Zhu, X.-Y.; Hatch, S. R.; Campion, A.; White, J. M. *J. Chem. Phys.* **1989**, *91*, 5011.

(9) Zhou, X.-L.; White, J. M. *J. Phys. Chem.* **1990**, *94*, 2643.

(10) Zhou, X.-L.; White, J. M. *Surf. Sci.*, **1991**, *241*, 259.

(11) Hatch, S. R.; Zhu, X.-Y.; White, J. M.; Campion, A. *J. Phys. Chem.* **1991**, *95*, 1759.

(12) Hanley, L.; Guo, X.; Yates, J. T., Jr. *J. Chem. Phys.* **1989**, *91*, 7220.

(13) Marsh, E. P.; Gilton, T. L.; Meier, W.; Schneider, M. R.; Cowin, J. P. *Phys. Rev. Lett.* **1988**, *61*, 2725.

(14) Radhakrishnan, G.; Stenzel, W.; Hemmen, R.; Conrad, H.; Bradshaw, A. M. *J. Chem. Phys.*, **1991**, *95*, 3930.

(15) Lamont, C. L. A.; Conrad, H.; Bradshaw, A. M. *Surf. Sci.* **1993**, *280*, 79.

(16) Van Duyne, R. P. In *Chemical and Biochemical Applications of Lasers*; Moore, C. B., Ed.; Academic: New York, 1979; Vol. 4.

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

(18) Gersten, J.; Nitzan, A. *J. Chem. Phys.* **1981**, *75*, 1139.

(19) Das, P. C.; Puri, A.; George, T. F. *J. Chem. Phys.* **1990**, *93*, 9106.

(20) Craighead, H. G.; Glass, A. M. *Opt. Lett.* **1981**, *6*, 248.

(21) Garoff, S.; Weitz, D. A.; Gramila, T. J.; Hanson, C. D. *Opt. Lett.* **1981**, *6*, 245.

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

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

(24) Garoff, S.; Weitz, D. A.; Alvarez, M. S. *Chem. Phys. Lett.* **1982**, *93*, 283.

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

(26) Chen, C. J.; Osgood, R. M. *Phys. Rev. Lett.* **1983**, *50*, 1705.

(27) Myli, K. B.; Coon, S. R.; Grassian, V. H. To be submitted.

(28) Chen, C. K.; de Castro, A. R. B.; Shen, Y. R. *Phys. Rev. Lett.* **1981**, *46*, 145.

(29) Zhou, X.-L.; White, J. M. *J. Chem. Phys.* **1990**, *92*, 5612.

(30) Feulner, P.; Menzel, D. *J. Vac. Sci. Technol.* **1980**, *17*, 662.

(31) We are following a similar roughening procedure to that used in ref 22.

(32) Burgess, D. Jr.; Stair, P. C.; Weitz, E. *J. Vac. Sci. Technol. A* **1986**, *4*, 1362. The optical constants for Ag change quite a bit between 400 and 320 nm. Of all the wavelengths and powers studied, the maximum temperature rise calculated was 15 K and, therefore, represents a worst case scenario. The calculations were done using the equations developed for smooth surfaces. To our knowledge, there are no methods available to calculate the temperature variation across a rough surface.

(33) A 1 ML covered surface is prepared by dosing multilayer quantities onto the surface and heating to remove the multilayer.

(34) Song, Y.; Gardner, P.; Conrad, H.; Bradshaw, A. M.; White, J. M. *Surf. Sci.* **1991**, *248*, L279.

(35) Because of adsorption from background 3-C_5H_4ClN during photolysis, there was multilayer desorption of 3-C_5H_4ClN in postirradiation TPD. Adsorption from background 3-C_5H_4ClN occurs whether or not the sample is irradiated, thus ruling out clustering effects due to irradiation.

(36) It is presumably the 3,3′-bipyridyl isomer that is being mass detected.

(37) From this result, we can rule out the possibility that slow thermal chemistry during the 2-h photolysis (instead of photon-induced chemistry) is the cause of product formation.

(38) *The Sadtler Standard Spectra*, Sadtler Research Laboratories, 1980.

(39) Ukraintsev, V. A.; Long, T. J.; Gowl, T.; Harrison, I. *J. Chem. Phys.* **1992**, *96*, 9114.

(40) Saas, J. K.; Laucht, H.; Kliewer, K. L. *Phys. Rev. Lett.* **1975**, *25*, 1461.