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Enhanced Photofragmentation on a Silver Surface

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Abstract

Photofragmentation has been observed for molecules near a roughened Ag(110) surface using low intensity UV excitation at 363.8 nm. The effect shows a nonlinear dependence on illumination intensity at intensities less than 100 W/cm^2 , and is dependent on molecule-surface separation.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

The unique properties of silver surfaces have provided large enhancements in linear phenomena such as Raman scattering¹ and in nonlinear phenomena such as second harmonic frequency generation². It has been predicted that such surfaces should also provide enhanced absorption and enhanced photochemistry for surface adsorbed molecules.³ We present here evidence for surface-enhanced photodecomposition of certain aromatic molecules using low intensity UV radiation at 363.8 nm.

Photofragmentation and observation of fragmented molecules were accomplished simultaneously in our experiments with the same excitation source (Ar⁺ ion laser, 363.8 nm, 20 mW). The UV line was used to decompose and to obtain surface Raman spectra of molecules condensed at 90K on a roughened Ag(110) surface under UHV conditions. The relative number of molecules fragmented by the UV radiation was deduced from the intensity of the 1600 cm⁻¹ amorphous carbon⁴ Raman band. The sensitivity of this method of detection is due to the high Raman cross-section of carbon⁵ and enhancement of the Raman signal by the roughened silver surface.

The surfaces used in this study were single crystal silver roughened by sputtering with Ar (5×10^{-5} Torr, 2 kV) at room temperature. Characterization of the surfaces by scanning electron microscopy revealed the presence of approximately 100 nm diameter conical features due to sputtering. The surfaces gave a Raman enhancement of about 1000X for pyridine ring breathing modes with 514.5 nm excitation for molecules immediately adjacent to the surface. An estimate of surface heating from a calculation⁶ based on surface optical dielectric properties determined by ellipsometry⁷ shows a temperature rise at the surface under steady state conditions of less than one degree for the laser powers and focussing conditions used.

Irradiation of adsorbed species on the silver surface at 363.8 nm

produced a molecule-dependent and coverage-dependent carbon Raman signal. Molecules for which this feature has been studied are listed in table I, together with information on electronic energy levels. It may be seen from this data that a common feature of the molecules that exhibit surface photofragmentation is the presence of an $n\pi^*$ triplet state lying below the energy of the laser at 27488 cm^{-1} . A possible explanation of surface photofragmentation is then enhanced singlet $\rightarrow$ triplet absorption followed by reaction from the triplet state (perhaps via a diradical intermediate^{8,9}). Extrapolation of the triplet lifetime measurements of Whitmore et al.¹⁰ for pyrazine near a silver surface to short distances gives a triplet lifetime which should be long enough for unimolecular photochemistry to occur.

The alternative to this is enhanced multiphoton absorption leading to ionization and fragmentation of molecules near the silver surface. Studies of gas phase multiphoton ionization¹¹ indicate that intensities of $>10^5\text{ W/cm}^2$ (aniline) or $>10^6\text{ W/cm}^2$ (benzene) are necessary to observe fragmentation of molecules at wavelengths of resonant two-photon absorption. The UV intensities used in our experiments (20 mW focussed to $7\times 10^{-5}\text{ cm}^2$, giving an intensity of $\sim 300\text{ W/cm}^2$) are several orders of magnitude lower than these figures, indicating that large enhancements of multiphoton absorption cross-sections would be required to explain the observed decomposition rates. Some support for this idea can be offered. Preliminary results indicate a nonlinear dependence of the initial rate of pyridine decomposition on photon flux ($n\sim 2.5$ photons/molecule) at intensities less than 100 W/cm^2 . At higher intensities a saturation of rate is seen. The ionization of the molecules studied would be expected to be a three photon process at the wavelength used (see table I).

The dependence of reaction rate on distance from the silver surface was

also investigated by simple coverage experiments and by using a spacer layer of NH_3 molecules. A monotonic increase in reaction rate with coverage was observed for pyridine between 5 and 50L (~1 and 10 monolayers). Careful measurements of carbon peak rate of change for a monolayer of pyridine on a 10L NH_3 spacer layer showed an initial rate of change half that observed for a monolayer of pyridine adjacent to the surface. The coverage dependence of surface enhanced Raman scattering on a similar surface with visible excitation (514.5 nm) shows that the Raman enhancement for the layer of molecules closest to the surface is at least 10X that of subsequent layers.¹² Thus the distance dependence of photodecomposition is clearly much longer ranged than that of surface Raman enhancement.

The identity of some of the molecule fragments observed may be ascertained from Raman vibrational frequencies. Shown in fig. 1 is the spectrum of 5L pyridine with 363.8 nm excitation. Although surface enhancement of Raman signal is not nearly as large with UV as with visible excitation (residual molecular pyridine peaks other than the 990 cm^{-1} band which are visible with 514.5 nm excitation are not visible in this spectrum), several peaks in addition to the carbon peaks at 1300 cm^{-1} and 1600 cm^{-1} are observed. CH stretching modes are seen at 3150 and $\sim 2850\text{ cm}^{-1}$, and a peak at 2195 cm^{-1} has been assigned to a CN vibration. CN is a likely initial product in the fragmentation of $\text{C}_5\text{H}_5\text{N}^+$.¹³

In conclusion, photodecomposition has been observed for several molecules near rough silver surfaces. The dependence on excitation intensity is nonlinear at low intensities (<100 mW), and the effect is dependent on molecule-surface separation. Further experiments are underway to determine the exact nature of the excitation and fragmentation process.

During the course of this work it was learned that multiphoton

photofragmentation has also been observed for high intensity excitation of pyridine on polycrystalline silver surfaces at 532 nm.¹⁴

Acknowledgements: This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U. S. Department of Energy under Contract Number ~~DE-AC03-76SF00098~~.

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Figure Captions

Table I.: Molecules examined for surface photofragmentation with low intensity UV irradiation at 363.8 nm.

Figure 1.: Raman spectrum of 5L pyridine on a rough silver surface using 363.8 nm excitation (40 min spectrum, 12 cm^{-1} resolution).

Table I

	<u>S₁ (cm⁻¹)</u>	<u>T₁ (cm⁻¹)</u>	<u>I_p (cm⁻¹)</u>	<u>Photofrag.</u>
Benzene	37800	29470	74580	no
Pyridine	34430	*	77990	yes
Pyrazine	30610	26560	77670	yes
Cyclohexane	60600	-	-	no
Cyclohexanone	35090	25800	-	no
Acetophenone	27560	25740	-	no
Benzaldehyde	26960	25195	77260	yes

lowest pyridine triplet seen in absorption spectrum is $^3\pi\pi^$ at 29650 cm⁻¹; however there is thought to be a $^3n\pi^*$ at lower energy¹⁵

Figure 1

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