

LASER DESORPTION MASS SPECTROMETRY OF SURFACE-ADSORBED MOLECULES

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The role of the electronic-plasma-resonance absorption of surface microstructure in the visible and UV pulsed laser desorption of adsorbates on a silver surface is examined. It is shown that the surface microstructure aids in the absorption of a significant fraction of the laser radiation and can lead to a relatively gentle thermal desorption of molecular monolayers adsorbed on the metal. This substantially increases the sensitivity and selectivity of time-of-flight mass spectrometry in the analysis of adsorbates on the metal surface.

Recently there has been much interest in the influence of small-scale metal microstructures on the properties of surface-adsorbed molecular overlayers. Rough metal surfaces have been shown to have a strong influence on the optical scattering processes of adsorbed molecules, both linear [1] and non-linear [2], the rate of photochemistry of adsorbed molecules [3], and the infrared laser induced desorption of adsorbed molecules [4]. In this letter we show that these same microstructures also have a strong and potentially important effect on the laser desorption of molecular overlayers using pulsed visible lasers. High-power pulsed visible lasers have been widely used as an analytical probe of small volumes of materials [5–8]. It is generally believed that the high-power pulse heats the material it is incident upon, creating a microplasma and ionizing a small volume of the material [9]. These ions can then be collected and analyzed with time-of-flight (TOF) mass spectrometry. However, while this technique is very sensitive, it suffers from two problems

which have heretofore precluded its widespread application to surface adsorbates [10,11]. First the relatively high powers necessary tend to vaporize a substantial amount of the material, making the separation of the bulk and surface species difficult, and second, the high powers used tend to fragment the molecular species being analyzed, complicating the identification of the parent molecules. We show that both these shortcomings can be minimized by taking advantage of the unique optical properties of surface microstructures. We are able to desorb and analyze a small fraction of a surface adsorbed monolayer, and we show that the adsorbate can be laser desorbed sufficiently gently that the parent ion is the predominant species. This is potentially a powerful and general technique for the analysis of surface adsorbates.

The samples studied were silver island films of 50 Å mass thickness produced by thermal evaporation at 1 Å/s onto polished quartz substrates heated to 150°C. The films consisted of islands, roughly circular in cross section, with a typical diameter of 200 Å, and covering 30–40% of the surface. After evaporation, the films were exposed to atmosphere and spin-coated from a solution of 10^{-3} mole/l paranitrobenzoic acid in

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ethanol. At this concentration, a monolayer of paranitrobenzoate is adsorbed onto the silver-island films [1]. The islands themselves formed the surface microstructures and these films exhibited excellent surface-enhanced Raman scattering (SERS) spectra from adsorbed molecules. The full optical behavior of these island films, and the role played by the microstructure in the anomalous optical scattering properties of adsorbates has been fully determined [1] and was well characterized by their absorption spectra [12]. A typical extinction spectrum, which has the same spectral behavior as the absorption, is shown in fig. 1.

We used a commercial laser desorption, time-of-flight (TOF) mass spectrometer which employs a Nd:YAG pulsed laser to vaporize and ionize the sample. The laser was equipped with harmonic generators to provide either 266 or 532 nm radiation with a pulse width of 10–15 ns. The laser beam was focused onto the sample by a 10X microscope objective. The laser energy density at the sample was estimated from the measured damage spot size on the film after a high-power shot and the total energy in the laser pulse measured with a calibrated calorimetric photometer. The ion collection optics are directly in line with the laser beam and, for this experiment, were several millimeters from the sample surface. This geometry required that the laser beam pass through the substrate and then the sample. The sample and TOF spectrometer were maintained at 1.3×10^{-3} Pa (10^{-6} Torr).

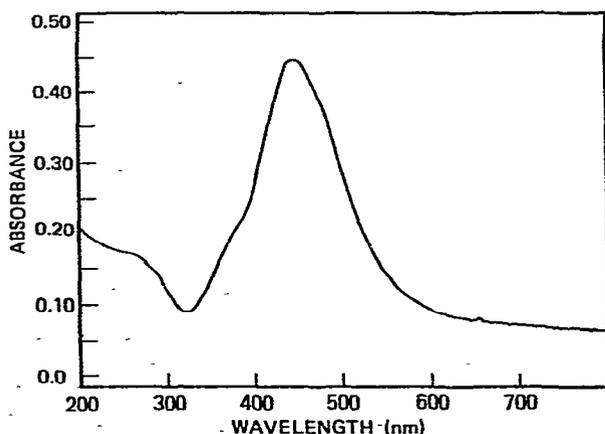


Fig. 1. Extinction spectrum of a 50 Å thick silver island film coated with a monolayer of paranitrobenzoate.

Using a tightly focused incident beam at 266 nm, energy densities of ≈ 0.5 J/cm² were achieved in a 14 μ m diameter spot. These powers were sufficient to cause marked ablation of the film, leaving a well-defined damage spot on which there appeared to be little or no silver remaining. Presumably most of the film material within the spot was vaporized, and the resulting TOF mass spectra contained strong Ag ion peaks in both the negative and positive ion spectra. Organic fragments were more prevalent in the negative current mode since proton liberation and molecular fragmentation usually generates negative ions [9]. A typical negative ion spectrum obtained from a bare (uncoated) Ag film is shown in fig. 2a. The primary peaks at 107 and 109 atomic mass units (amu) are due to the two silver isotopes. Several of the other peaks can also be readily identified. Those at 35 and 37 amu are due to Cl⁻ ions which presumably are left on the substrate during an HCl rinse in its cleaning. Peaks at 120 (Si₂O₃⁻), 76 (SiO₃⁻), and 60 (SiO₂⁻) amu can be attributed to material from the fused quartz substrate. The remaining peaks are due to unidentified impurities either in or on the silver itself or the quartz substrate. Their presence is not surprising, since the quartz substrate is subjected to numerous solvent rinses in the cleaning process prior to the film fabrication, and the silver films were routinely stored in air for a day or two prior to the laser mass spectra being taken.

The negative ion TOF mass spectrum of a silver-island film coated with a monolayer ($\approx 6 \times 10^{14}$ molecules/cm²) of paranitrobenzoate is shown in fig. 2b. It is nearly identical to that of the uncoated film in the position and relative intensities of the peaks, with few exceptions. These are the relatively weak peaks at 166, 122, and 46 amu, which can be respectively assigned to the parent paranitrobenzoate ion, (M-H)⁻, as well as the fragments of the parent minus the CO₂, (M-H-CO₂)⁻, and the NO₂ ion itself. Thus we are clearly detecting the presence of the organic surface adsorbate in the TOF mass spectrum of the desorbed ions. In contrast as shown in fig. 3, the positive ion spectrum had relatively few peaks, with virtually none of the impurity peaks and no evidence of the surface adsorbate. Instead, we observe the two Ag⁺ isotope peaks at 107 and 109 amu, as well as those peaks attributed to silver clusters, Ag₂⁺, centered at 216 amu. We also see small peaks at 151 and 153 amu which we attribute to (Ag + CO₂)⁺ complexes, and which are

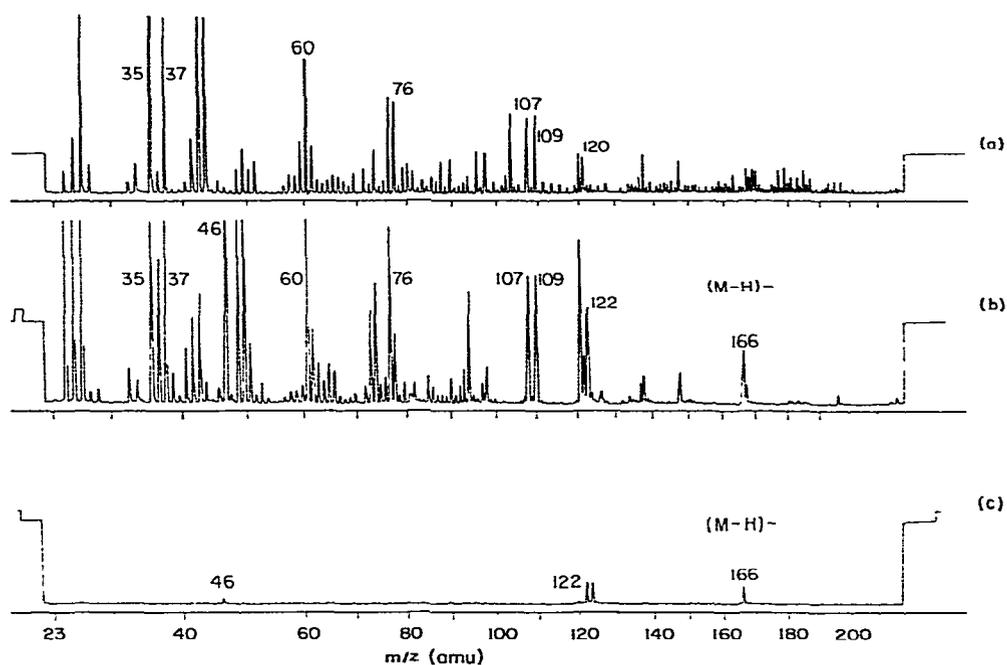


Fig. 2. Negative ion TOF mass spectra of (a) uncoated silver film. (b) paranitrobenzoate monolayer coated film at laser energy densities of $>400 \text{ mJ/cm}^2$ and (c) coated film at lower laser energy density, $\approx 95 \text{ mJ/cm}^2$. The laser wavelength was 532 nm for (a) and 266 nm for (b) and (c).

present to the same extent on both coated and uncoated films, implying that they are not due to the adsorbed paranitrobenzoate. Similar behavior, for both the positive and negative ion mass spectra and for both coated and uncoated films, was obtained when 532 nm radiation was used.

Although we are clearly able to detect the surface-adsorbed molecules, substantially better sensitivity to the specific organic adsorbate was obtained by reduc-

ing the energy density of the incident laser pulse. With the energy density decreased to $\approx 100 \text{ mJ/cm}^2$, all the peaks due to the silver, the substrate, and the impurities are no longer present in the negative ion spectrum, as shown in fig. 2c. Instead, the only peaks that remain are those at 166, 122, and 46 amu, due to the surface adsorbed paranitrobenzoate. Furthermore, fragmentation of the parent molecule is greatly reduced. At these low energy densities, visual inspection after the laser shot

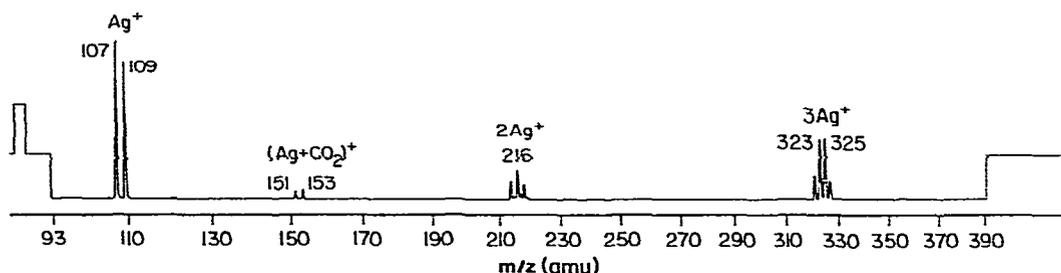


Fig. 3. Positive ion spectrum of a paranitrobenzoate-coated silver island film with laser energy density of $>400 \text{ mJ/cm}^2$ and wavelength of 532 nm.

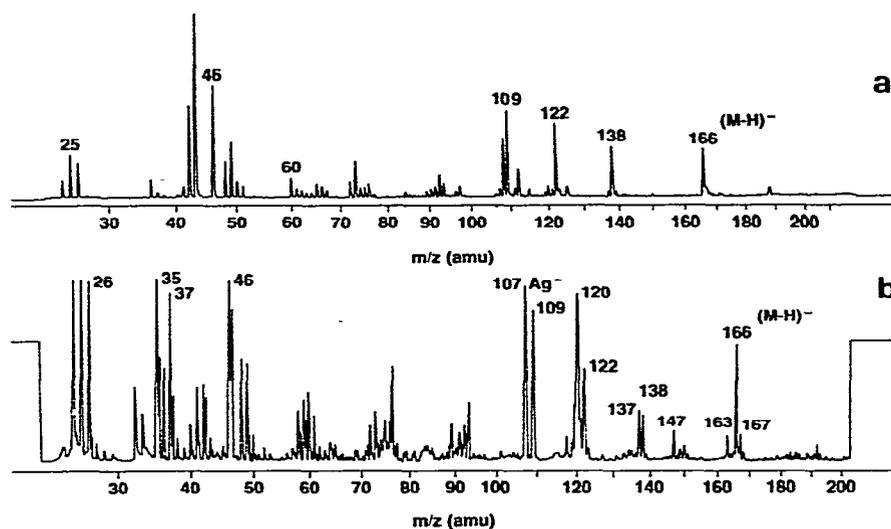


Fig. 4. Negative ion TOF mass spectra of (a) paranitrobenzoic acid crystals and (b) paranitrobenzoate adsorbed on a relatively smooth silver surface. Both spectra were obtained with 266 nm excitation.

shows only a very slight change in the optical appearance of the film rather than the pronounced damage spot observed at higher powers. In addition, identical TOF spectra of the adsorbed paranitrobenzoate could be obtained from the same spot with ≈ 5 successive laser pulses, suggesting that $\approx 10^9$ molecules are desorbed each shot. Irradiation of an uncoated film at similar energy densities gave only the Ag peaks in the TOF spectrum, with no impurities or adsorbates observable.

For comparison, TOF mass spectra of crystals of paranitrobenzoic acid were obtained, as shown in fig. 4a. While the molecule in the bulk crystal is slightly different than the surface-adsorbed species, and may have a different fragmentation pattern, the spectra show considerably more impurity and fragment peaks than those of the surface-adsorbed molecules obtained with low powers from the silver islands. To confirm the critical role of the surface microstructure, we also obtained TOF mass spectra from laser-desorbed paranitrobenzoate adsorbed on a relatively smooth silver surface. A monolayer of paranitrobenzoate was adsorbed on a TEM grid coated with a thick layer of silver or on a piece of silver shot and the exciting laser was aligned to impinge on the edge of the sample. A typical spectrum is shown in fig. 4b for 266 nm excita-

tion, and is very similar to the TOF spectra of the coated island films obtained with high powers. However, when the laser power was reduced, we were unable to obtain the same impurity-free TOF spectra of paranitrobenzoate from the smooth surface that were obtained from the silver islands. These results demonstrate that the surface microstructure both increases the sensitivity of the laser desorption mass spectra to surface adsorbed molecules and reduces the parent ion fragmentation.

While thermal laser desorption mass spectrometry does not require a rough silver surface [10], the existence of the microstructure certainly can improve the sensitivity of the technique to adsorbates on the metal surface. To determine the role of the electronic plasma resonances of the surface microstructure in the desorption process, we measured the dependence of the strength of the paranitrobenzoate ion peaks on the incident laser power density. We found that the threshold powers for desorption, as well as the power dependence of the signal at low energy densities were identical at 266 and 532 nm excitation, to within our experimental accuracy. On these island films, all the incident power is absorbed in the silver islands themselves, and from the measured absorption spectrum, we find that the fractional absorption in the films is approximately the

same at both 266 and 532 nm. In contrast, from the studies of the optical scattering of adsorbates on these films, we know that the strength of the local electromagnetic field at the surface of the islands is, on average, considerably stronger at 532 nm than at 266 nm. In fact, using the same model that accounts for the excitation spectrum of SERS on these island films [12], we can estimate that the local field strength at the island surface for 532 nm radiation is, on average, ≈ 50 times greater than for 266 nm radiation.

The fact that we observe no increase in the efficiency for laser desorption at 532 nm compared to 266 nm precludes any desorption mechanism which depends on the strength of the local field at the surface adsorbed molecule. Instead, the desorption mechanism is most likely purely thermal in nature, and results from the heating of the silver islands. This apparently causes the surface-molecule bond to break first, since it is weaker than the silver-silver bonds of the metal. The weaker bond strength is indeed born out by the observation that the SERS signal disappears when the coated films are heated above 250°C, presumably because of desorption of the surface-adsorbed paranitrobenzoate [13]. The role of the silver surface microstructure in the desorption process is two-fold. It serves to improve the penetration of the electromagnetic field into the silver, allowing a more efficient absorption of the incident laser power. Furthermore, the surface roughness tends to localize the thermal energy in the vicinity of the adsorbates, rather than heating the bulk substrate as would occur for a smooth surface. The combination of these effects leads to the observed improvement in the thermal desorption of the surface adsorbates and in the resulting TOF spectrometry.

The thermal nature of the desorption process suggests that the use of surface microstructure is not limited to silver and could prove to be a rather general aid in applying this technique to the study of the molecular make-up of surface-adsorbed monolayers. The penetration of the laser field into any metal will be increased by surface roughness, and the heating which results should cause a similar improvement in the application of laser-

desorption mass spectrometry to the adsorbates. We note that this might prove particularly useful in the study of adsorbates on dispersed catalysts, where the laser power could be absorbed primarily in the metal particles, rather than the support, allowing selective desorption of adsorbates from the catalyst itself. Finally, since we are able to see signal from the adsorbate for many laser shots from the same spot on the film, and since the signal to noise is still relatively high, detection of submonolayer coverage of surface adsorbates should be quite feasible. This suggests that this technique has the potential of being an excellent and powerful analytical probe of the molecular nature of surface adsorbates.

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