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Surface sensitive detection of organic molecules using ion beam induced desorption

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Abstract: The ability to use energetic ion bombardment coupled with multiphoton resonance ionization to quantitatively detect molecules on surfaces has been investigated. Benzo(a)pyrene has been used to establish the resonant nature of the ionization process and to demonstrate the tunable fragmentation available with this type of ionization. Serotonin was then used to demonstrate the sensitivity of the method.

1. Introduction

Surfaces play a vital role in many important processes such as heterogeneous catalysis, friction, corrosion, adhesion, etc. One of the techniques commonly used to characterize surfaces is secondary ion mass spectrometry (SIMS). This technique uses the interaction of an energetic ion beam with a solid to cause ejection of secondary ions from the topmost atomic layer. These ions are then detected using a mass spectrometer.

While the SIMS technique has made many contributions to the understanding of various surface processes it has significant limitations when it comes to the quantitation of trace analytes. First, the secondary ions are only a small fraction of the material desorbed by the primary ion impact. The majority of this material is ejected as neutral species. For SIMS, this leads to inefficient sampling of the ablated material so that sensitivity is lost. Second, the probability that a particle will leave the surface as an ion, may vary by orders of magnitude depending on the surface composition, so that it is very difficult to obtain quantitative results (Kimock et al. 1984). In order to overcome these limitations, multiphoton resonance ionization (MPRI) has been combined with ion induced desorption. Laser ionization allows the sampling of the more abundant and less variable neutral component of the ejected flux which increases the analytical signal and makes it more quantitative. The selectivity of resonant ionization reduces noise, thereby enhancing sensitivity. It also is a very efficient means of ionization, allowing relatively large ionization volumes for a given laser power. Using this method, a detection limit of 9 parts per trillion for In atoms uniformly doped into Si has been obtained (Pappas et al.1989). It is not obvious, however, that similar results can be achieved when this technique is applied to the measurement of molecules on surfaces. For one thing, molecules have many rotational and vibrational levels so that there are larger densities of states with more populated levels than are observed for atoms. This reduces the selectivity of the ionization. Although the desorbed molecules could be cooled by entaining them in a supersonic jet expansion in order to reduce the number of populated levels (Grotemeyer et al. 1986), this entrapment would sacrifice sensitivity. Sensitivity can also be lost due to the fragmentation of the analyte. For this reason the resonant nature of the ionization is even more important when studying molecules, since the lower power densities that can be used will reduce the absorption of photons in excess of those needed for ionization, which frequently result in fragmentation. Single photon ionization can also avoid this fragmentation but it lacks

selectivity, and typically only small ionization volumes can be used which reduces sensitivity (Schule et al. 1988).

In this work, we examine polycyclic aromatic hydrocarbons (PAH's) as initial specimens for molecular detection because they absorb strongly in the near UV at easily attained energies. These energies are sufficient such that two photons will exceed the ionization potential of the molecule. PAH's are also important pollutants with real world trace measurement problems. Initial experiments involve the investigation of the power dependence of the signal. Moreover, the increased sensitivity relative to SIMS, is demonstrated for benzo(a)pyrene. Finally, the linearity and limits of detection are investigated for serotonin, a biologically important molecule.

2. Experimental

The apparatus has been described in detail elsewhere (Kimock et al. 1984, Pappas et al. 1989). All experiments are performed in an ion pumped Perkin-Elmer Utek TNB-X ultra high vacuum chamber with a base pressure of 5×10^{-9} torr after bakeout. The system is equipped with a load-lock pumped by a Balzers Model TSU 170 liter/sec turbomolecular pump for fast sample insertion. A 5.6 μs pulse of primary Ar^+ ions (34 μA, 10 keV) generated by a Physicon Model DP10-01 duoplasmatron source is focused to a 1 mm diameter spot on the sample at a 45° angle of incidence. The laser system consists of a Quanta-Ray Model PDL-2 dye laser pumped by the second harmonic of a Quanta-Ray Model DCR-2A Nd:YAG laser with a 30 Hz repetition rate. The dye laser produces visible 590 nm light with Exciton Rhodamine 590/methanol dye solutions and this light is frequency doubled with a Quanta-Ray Model WEX-1 wavelength extension unit to produce 280 nm UV light. While the output characteristics vary from alignment to alignment, some typical values are: 5 mJ/6 ns pulses of light with a beam area of 0.5 cm^2 (1.6×10^6 W/cm^2). The laser is triggered ~150 ns after the end of the primary ion pulse, with the resultant ions being extracted into a reflecting time-of-flight (TOF) mass spectrometer with a pulsed extraction field. The reflecting potentials can be optimized to pass either photoions or secondary ions to a Galileo Electro-Optics Corp. Model FTD 2002 dual microchannel plate (MCP) detector. The output signal from the MCP is processed with a Stanford Research Systems Model SR 250 gated integrator for power dependence studies and ion fraction measurements. Mass spectra are recorded by sending the MCP signal to a 100 MHz Digital Signal Processing Technology (DSP) Model 2001AS transient recorder with summing memory. The instrument is interfaced to a Digital Equipment Corp. MicroVax II computer using CAMAC technology.

For the experiments involving pyrene and benzo(a)pyrene, bulk samples were used since sensitivity was not an issue. These chemicals were obtained from Aldrich Chemical Company and used without further purification. Milligram quantities were dissolved in benzene and deposited onto an ultrasonically cleaned substrate attached to a Cu backplate. The pyrene samples were evaporated onto polycrystalline Au foils whereas the benzo(a)pyrene was deposited onto pieces of {100} Si wafers. These samples were allowed to air dry before being inserted into the chamber. Serotonin was obtained from Sigma Chemical Company and used without further purification. The serotonin samples were prepared in HPLC grade water and deposited onto Si substrates at which point the solvent was vacuum evaporated in the load-lock. For the quantitative studies a series of standards ranging in concentration from 10^{-4} M to 10^{-7} M were prepared by quantitative dilution of a 10^{-3} M stock solution. 10 μl aliquots of these standards were analyzed where the amount of serotonin in the analysis zone varied between 5×10^{-11} to 5×10^{-14} moles. Each concentration was repeated three to four times to provide independent analysis.

3. Results

Previously we have demonstrated that carbazole gives a large molecular ion signal when desorbed as neutral molecules that are ionized with two 287 nm photons (Winograd 1988).

Similar results were obtained with pyrene and benzo(a)pyrene at 280 nm (Hrubowchak et al. 1990). When the power dependence at 280nm of the benzo(a)pyrene signal was investigated, results very similar to those for pyrene were obtained. Below 5 x 10^5 W/cm^2 the dependence is linear indicating a one photon dependence, presumably because the resonant excitation step is saturated. At power densities above 1 x 10^6 W/cm^2 the signal drops with increasing power due to fragmentation caused by the absorption of additional photon(s) by the parent ion. The ability to control the amount of fragmentation by varying the laser power allows one to choose between optimum sensitivity or the extraction of structural information simply by changing the laser power (Boesl et al. 1987). This tunable fragmentation is illustrated in Figures 1 and 2. In Fig. 1 the laser power density is 3 x 10^5 W/cm^2. This yields a clean spectra that is dominated by the parent ion. Conversely, in Figure 2 where the power density is 2 x 10^6 W/cm^2, the molecular ion peak is diminished in favor of different fragment peaks characteristic of the structure of the parent molecule. When we compare the benzo(a)pyrene MPRI signal in Figure 1, which is in excess of 250 mV, to the less than 0.1 mV SIMS signal obtained on the same instrument, we see that it is advantageous to sample the neutrals when sensitivity is important. This is not surprising since we have previously shown that at least 98% of desorbed pyrene leaves the surface as neutral molecules (Hrubowchak et al. submitted).

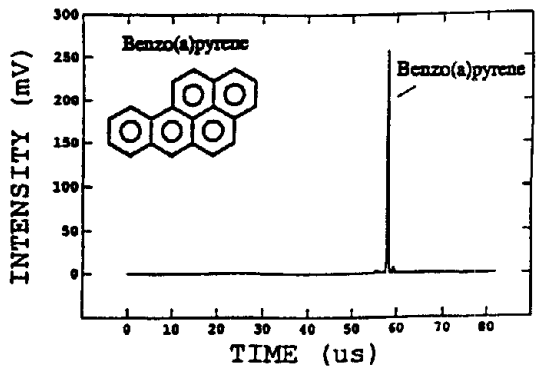

Fig. 1. Time-of-flight MPRI spectrum of benzo(a) pyrene taken at 280 nm with a laser power density of 3 x 10^5 W/cm^2.

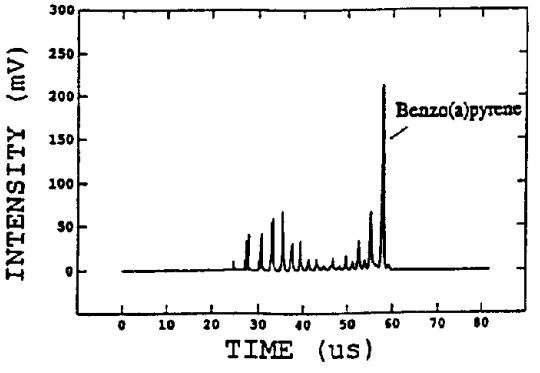

Fig. 2. Time-of-flight MPRI spectrum of benzo(a)pyrene taken at 280 nm with a laser power density of 2 x 10^6 W/cm^2.

When MPRI with 280 nm light is applied to serotonin, a very important biomolecule, the mass spectrum in Figure 3 is observed. As can be seen from the spectrum, the base peak is the parent ion less CH_2NH_2 from the side chain. It is interesting to note that this is also the base peak in the electron impact mass spectrum of serotonin. The quantitative nature of the laser signal is demonstrated in Figure 4. Here the log of signal intensities are plotted against the log of the number of molecules sampled by the ion beam. Before the individual signal intensities at a given concentration are averaged, they are normalized to the laser power and primary ion current used during their measurement. The result is a line of slope 0.946 ± 0.031 and a correlation coefficient of 0.996. A detection limit is calculated by measuring the signal to noise ratios (S/N) from spectra and extrapolating to a concentration that would give a S/N of 2. This extrapolated concentration is then normalized to 100 μA of obtainable ion current with the result being averaged with the results from other runs and other concentrations. This yields a detection limit of 5.2 x 10^{-15} moles ± 20% for serotonin. This compares to a detection limit of 6.4 x 10^{-16} moles for pyrene (Hrubowchak et al. submitted). The difference between the two probably results from differing ionization efficiencies and the fragmentation that takes place in the serotonin's case.

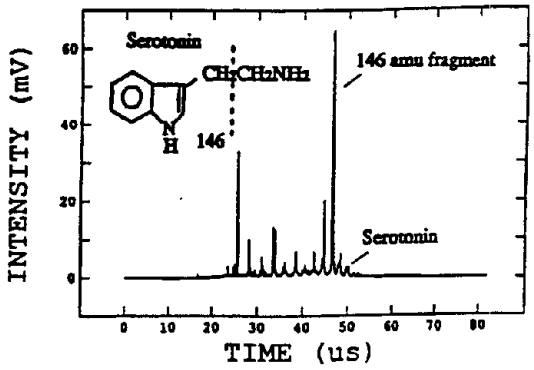

Fig. 3. Time-of-flight MPRI spectrum of serotonin taken with 280 nm light.

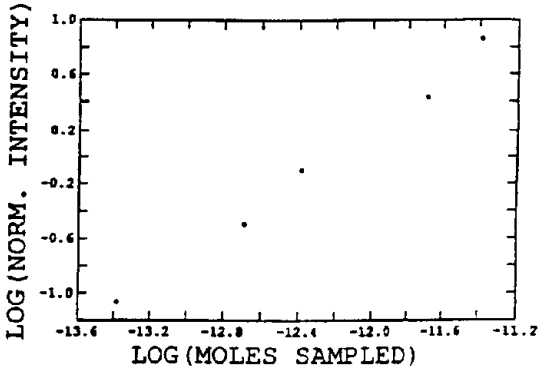

Fig. 4. Log-log plot of 146 amu serotonin fragment intensity versus the number of moles of serotonin sampled by the ion beam.

4. Conclusion

We have demonstrated that energetic ion bombardment coupled with MPRI can be used to sensitively and quantitatively detect submonolayer quantities of molecules on surfaces. The ionization process has been shown to be resonant by the power dependences observed. The resonant nature of the ionization process is important because it increases the sensitivity of the method, as compared with nonresonant ionization, through the increased spacial overlap and decreased fragmentation that comes from efficient ionization at low power densities. Resonant ionization also increases sensitivity by lowering noise that would degrade the S/N ratio. In addition, we have shown that this method can be applied to biological molecules which are typically fragile molecules. Serotonin, which served as a test case for biomolecules, yielded a linear calibration curve with a detection limit of 5.2×10^{-15} moles. We are currently applying this method to the detection of molecules in complex matrixes.

5. Acknowledgement

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