

WHAT ARE THE LIMITS OF DETECTION FOR MOLECULES ON SURFACES USING ION BEAM INDUCED DESORPTION?

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Our research has been focused toward the use of multiphoton resonance ionization (MPRI) spectroscopy to selectively ionize desorbed neutral atoms. This approach has three important consequences: (i) the ionization efficiency can approach 100% in favorable cases, (ii) ionization is selective to the desired element and a function of the excitation wavelength of the laser and (iii) high laser powers are not required, meaning that the ionization volume, as defined by the size of the laser, can be quite large. These three factors allow for extremely high sensitivity measurements for atoms. We have recently reported detection limits for In uniformly doped into Si of just a few hundred atoms spread over 1 cm².¹

Is it possible to extend these measurements to molecules and achieve the same level of performance? The answer to this question is not obvious since molecular species possess a high density of states and the MPRI process can be quite complex. In earlier experiments, several groups have used laser desorption to inject nonvolatile molecules into supersonic jets of Ar atoms or CO₂ molecules.^{2,3} This jet ensures that all the molecules will be in their ground states and that the spectroscopy will be well-defined. This approach yields elegant spectral quality but suffers in sensitivity. Another group has successfully employed MPRI to ionize molecules directly as they exit a capillary gas chromatographic (CGC) column.⁴ These workers obtained excellent molecular ion signals on many molecules without using a supersonic jet expansion. In this work we present initial experimental results for the detection of neutral pyrene molecules desorbed from a gold surface by ion bombardment using MPRI detection. The results suggest that small fractions of a monolayer are easily detectable.

Pyrene was selected on the grounds that: (i) it exhibits a strong $\pi \rightarrow \pi^*$ transition (as an absorbing chromophore) in the near UV, (ii) it has an ionization potential of 7.42 eV⁵ such that 2 photons of 280 nm radiation will resonantly photoionize the molecule, and (iii) pyrene has been detected and quantitated using CGC/MPRI⁴ which can serve as a benchmark analysis for comparison.

The use of MPRI to detect neutral pyrene molecules desorbed from a Au surface is shown in Fig. 1a. The most important point to note is the large molecular ion

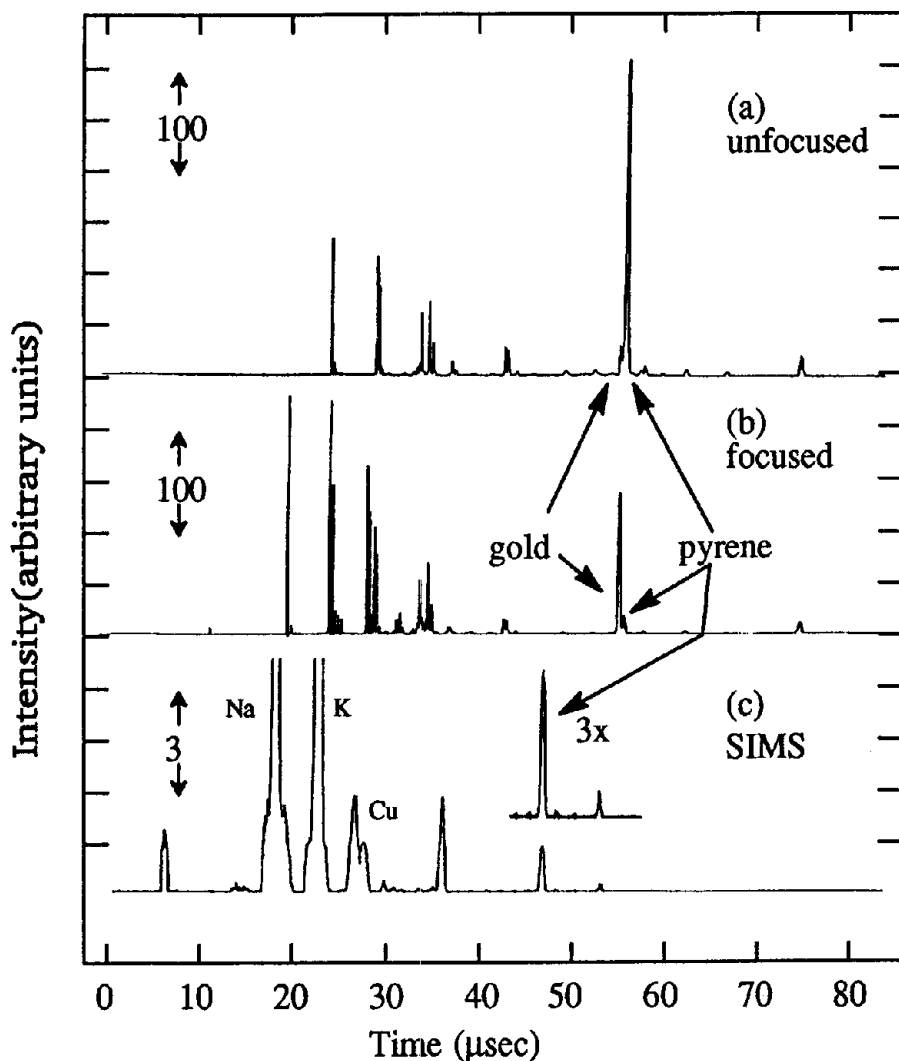


Fig. 1. Time-of-flight MPRI spectrum of pyrene indicating the molecular ion at 202 amu for an (a) unfocused and a (b) tightly focused laser beam. The TOF-SIMS spectrum using a 510 ns Ar^+ ion pulse is shown in (c). The time scale is somewhat arbitrary. The ion pulse occurs at $\sim 3 \mu\text{s}$, and the laser is activated after 9 μs . Masses are then computed from known elements.

signal with control over photofragmentation. For Fig. 1(a), the laser was tuned to 280 nm and operated at a power density of $4.1 \times 10^7 \text{ W/cm}^2$ for an unfocused 8.8 mm diameter laser beam. However, upon focusing the beam to 0.635 mm ($5.2 \times 10^9 \text{ W/cm}^2$) to induce nonresonant ionization, extensive photofragmentation was observed as demonstrated in Fig. 1(b). The molecular ion signal dropped by a factor of ~ 20 commensurate with an increase in intensity of various low mass hydrocarbon fragments.

In an effort to compare SIMS and the MPRI method directly, the ion reflector potentials were reoptimized for secondary ion detection. A TOF-SIMS spectrum of bulk pyrene is shown in Fig. 1c. Along with the ubiquitous Na and K secondary ions, a pyrene signal of low intensity is observed. The molecular ion signal obtained by MPRI is clearly much greater than that obtained by SIMS. We have measured the "ion fraction" for pyrene desorbed from a Au substrate by boxcar averaging the postionized neutral and ionic pyrene analog signals. After several corrections to the data (such as a laser spatial overlap factor, an integrated ion pulse area factor, and subtraction of a gas phase component from the neutral signal), we measured a pyrene ion fraction of $\sim 1.7 \times 10^{-2}$. This value does not include a correction for the ionization efficiency of pyrene by MPRI. Thus, the vast majority of the desorbed molecules eject from the surface as neutrals. This fact is a major driving force for applying MPRI to trace analytical problems where efficient sampling is an issue as a means of increasing sensitivity.

The power dependence of the laser ionization signal is shown in Fig. 2. At

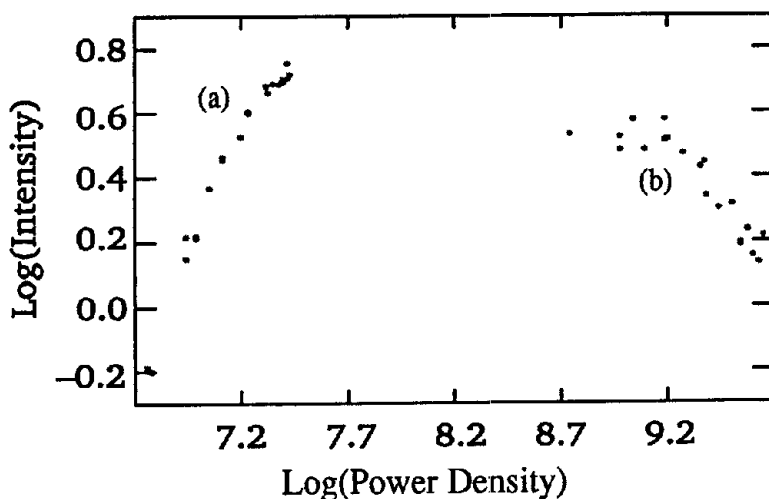


Fig. 2. Log-Log dependence of the pyrene molecular ion intensity as a function of laser power density for an (a) unfocused and a (b) tightly focused laser beam.

low power density, the ionization signal exhibits a 1-photon dependence (the slope of the normalized linear plot is 1.2). Interestingly, the intensity reaches a plateau region at a power density of $\sim 2.3 \times 10^7$ W/cm². The 1-photon dependence suggests saturation of the resonant excitation and nonsaturation of the ionization step. The MPRI process for this spectroscopically complex system exhibits little or no molecular ion photofragmentation. However, for a tightly focused beam, the molecular ion intensity exhibits a plateau region from $\sim 5 \times 10^8$ W/cm² to $\sim 1.7 \times 10^9$ W/cm² followed by a rapid decline in intensity. In this regime, extensive photofragmentation to low mass hydrocarbon moieties is observed.

It is important to know if 100% ionization efficiency is being achieved given the functional dependence of Fig. 2(a). An estimate of this efficiency can be calculated using analog data and/or pulse-counting measurements. From the analog data, the signal amplitude of the bulk pyrene sample was 520 mV with a 250 ns peak width. At the working voltages, the dual microchannel plate detector has a specified gain of 1.2×10^7 generating ~ 1400 pyrene molecular ions/laser pulse. Inserting this value into a sensitivity equation described elsewhere,⁶ an ionization efficiency of $3 \times 10^{-3}\%$ was obtained. In order to obtain a more accurate value of the ionization efficiency, a $1 \mu\text{L}$ aliquot of a 10^{-5} M pyrene/methanol solution was deposited onto the surface of a Au substrate. The relative surface concentration of pyrene in the sampling area (for an ion beam diameter of 3 mm) is at most $\sim 3.8\%$, although there are presently large uncertainties in this number. The average count rate for 3 different targets of the same pyrene concentration was found to be 2.4×10^4 counts for a 5 minute counting period. Inserting this value into the same sensitivity equation yields a lower limit of the ionization efficiency of $7.5 \times 10^{-4}\%$, in reasonable agreement with the bulk analog data.

Given the above information, what are the limits of detection for molecules on surfaces using ion beam induced desorption? The sensitivity for these measurements was determined using the results of the analysis for the 4.5×10^{-12} mole pyrene on Au samples. The 3 independent targets yielded an average of 2.4×10^4 signal counts and 15 background counts during the 5 minute counting period for a primary ion current of 11.5 μA and an ionization efficiency of $\sim 1 \times 10^{-3}\%$. Thus, for a signal-to-noise (S/N) level of 2, the concentration of the 4.5×10^{-12} mole sample may be extrapolated to 5.6×10^{-15} moles. This implies that for an obtainable incident ion current of 100 μA , the detection limit is 6.4×10^{-16} moles. Clearly, the limiting factor of this detection limit is the low ionization efficiency most probably due to losses into uncharacterized fragmentation states either above or below the ionization potential of pyrene. Given the fact that we have recently demonstrated the detection of ~ 200 atoms of In present on 10^{15} atoms/cm² of a Si surface, the MPRI approach may be sensitive to as few as 200,000 molecules in the topmost layer of a substrate. This work was partially supported by NSF, the Office of Naval Research and the IBM Corporation.

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