

# Laser photoionization detection of submonomolecular surface films

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A new method has been developed for detecting ultrasmall numbers of molecules adsorbed on a surface ( $10^{-8}$ – $10^{-10}$  of a monolayer). The method involves a pulsed laser desorption of the adsorbed molecules, a subsequent resonant stepwise photoionization of these molecules above the surface by a UV laser beam, and the detection of the ions in a spectrometer. The method has been used to study anthracene and naphthalene adsorbed on graphite.

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The method of selective stepwise photoionization of molecules which has recently been developed<sup>1</sup> has opened up some new experimental possibilities for studying free polyatomic molecules in a beam or in the gas phase. The high efficiency and selectivity of resonant laser photoionization have made it possible to achieve a sensitivity corresponding to the detection of single molecules in the illumination volume.<sup>2</sup> An equally important problem is to detect polyatomic molecules adsorbed on a surface. The other high-sensitivity methods which are available—secondary ion mass spectrometry, for example—can detect numbers of molecules down to  $10^{-6}$  of a monolayer.<sup>3</sup>

In this letter we show that the sensitivity with which adsorbed polyatomic molecules can be detected can be improved significantly by combining stepwise laser photoionization with pulsed desorption of the molecules. In this approach, a first laser pulse, applied to the surface, desorbs the molecules, which are then ionized by one or several laser pulses at some distance from the surface. The use of pulsed desorption substantially reduces the decomposition of molecules upon heating,<sup>4</sup> and stepwise laser photoionization is in practice the only method available for ionizing desorbed molecules with a probability approaching unity.

One of the most important factors determining the sensitivity with which the adsorbed polyatomic molecules are detected in this method is the maximum fraction of molecules which can be desorbed from the surface without undergoing decomposition. In the present experiments we studied this question for the particular cases of naphthalene and anthracene molecules adsorbed on graphite.

The experimental apparatus consists of a time-of-flight mass spectrometer<sup>5</sup> with a graphite substrate at  $T = 200$  K, mounted on the ejecting electrode of an ion source, and synchronized pulsed lasers using  $\text{CO}_2$  molecules ( $\lambda = 10.6 \mu\text{m}$ ) and KrF molecules ( $\lambda = 248 \text{ nm}$ ). The beam from the  $\text{CO}_2$  laser strikes the substrate in an area of  $3 \times 3 \text{ mm}^2$  at an angle of  $7^\circ$ ; the ionizing beam from KrF excimer laser propagates parallel to the substrate, grazing its surface. The time delay between the desorbing and ionizing laser pulses is  $0.7$ – $1 \mu\text{s}$ .

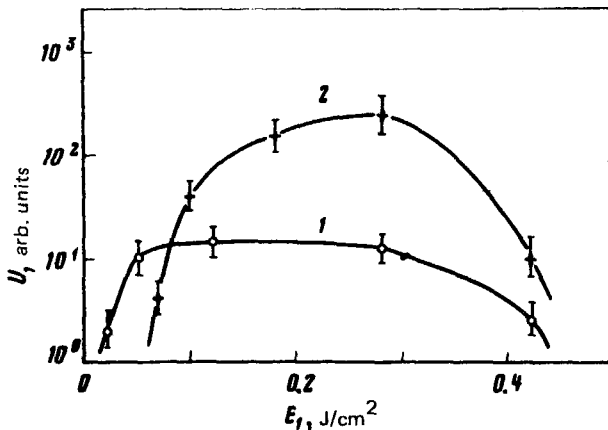


FIG. 1. Desorption ( $U$ ) of naphthalene molecules (curve 1) and anthracene molecules (curve 2) from a graphite surface vs the energy density  $E_1$  of the beam from the CO<sub>2</sub> laser. The energy density of the ionizing beam from the KrF laser ( $\lambda = 248$  nm) is  $E_2 = 1.5 \times 10^{-2}$  J/cm<sup>2</sup>.

The naphthalene and anthracene molecules are deposited on the substrate from the gas phase and are at equilibrium with the corresponding vapor at partial pressures  $10^{-12}$ – $10^{-13}$  Torr (according to estimates based on the photoionization measurements). The time between successive laser pulses is chosen to be 5–10 s, longer than the characteristic time for relaxation to an equilibrium concentration of molecules on the surface.

The naphthalene and anthracene molecules desorbed by the IR beam are photoionized by the UF pulse from the KrF laser through intermediate, electronically excited states. The energy of two photons,  $2\hbar\omega = 10$  eV, is sufficient to ionize either molecule. According to Ref. 2, the efficiency of the ionization of naphthalene molecules reaches 100% at energy densities of 0.2–0.3 J/cm<sup>2</sup> from a KrF laser. In the present experiment, however, because of the strong photoionization signal—which goes beyond the linear region of the electron multiplier, the molecules are ionized by pulses with an energy density of 0.015 J/cm<sup>2</sup>, and the corresponding ionization efficiency is about 2% (Ref. 2).

Figure 1 shows the photoionization signal of the naphthalene and anthracene molecules vs the energy density of the CO<sub>2</sub> laser pulses that bombard the surface. The desorption signal has a plateau at energy densities 0.05–0.3 J/cm<sup>2</sup> in the case of the naphthalene molecules and 0.15–0.3 J/cm<sup>2</sup> in the case of the anthracene molecules. The maximum ion signal observed experimentally consisted of about 10<sup>3</sup> ions/pulse (naphthalene) or 10<sup>4</sup> ions/pulse (anthracene). At IR energy densities above 0.3 J/cm<sup>2</sup> we observed a sharp decrease in the yield of molecular ions, accompanied by the simultaneous appearance of various fragment ions and ions of the substrate material (C<sup>+</sup> and C<sub>2</sub><sup>+</sup>), in the cases of both anthracene and naphthalene. In this energy range we also observed an intense emission from the substrate, which demonstrated that the surface was heated to  $T \geq 1000$  K.

The rate  $W_{\text{des}}$  at which the molecules are desorbed from the surface is given by<sup>6</sup>

$$W_{\text{des}} = \Omega \exp(-E/kT), \quad (1)$$

where  $\Omega = 10^{12}$ – $10^{14} \text{ s}^{-1}$  is the characteristic vibration frequency of the molecules on the surface, and  $E$  is the binding energy with the surface. Saturation of the pulsed desorption corresponds to the condition

$$W_{\text{des}} \tau_p = \tau_p \Omega \exp(-E/kT) \approx 1. \quad (2)$$

A further increase in the surface temperature does not increase the photoion signal; this situation corresponds to the appearance of the plateau on the plot of the IR radiation vs energy (Fig. 1). In the case of naphthalene it is a simple matter to estimate the efficiency at which molecules on the surface are detected: With complete desorption of the molecules, the observed ion signal of  $10^3$  ions/pulse corresponds to a surface concentration of  $10^6$  molecules/cm<sup>2</sup> or about  $10^{-8}$  of a monolayer (here we are assuming a 2% efficiency for the ionization of the molecules by the UV pulse and a 50% efficiency for detecting the resulting ions<sup>2</sup>). The threshold for the detection of the adsorbed molecules at a signal level of 1 ion/pulse is 50–100 molecules/cm<sup>2</sup> at the optimum energy of the UV ionizing beam.<sup>2</sup>

Between a surface and a gas phase, the densities of molecules on the surface,  $n_{\text{srf}}$ , and in the gas,  $n_{\text{gas}}$ , are related by the simple equation

$$n_{\text{srf}} / \tau_{\text{ads}} = n_{\text{gas}} v_0/4, \quad (3)$$

where  $\tau_{\text{ads}} = 1/W_{\text{des}}$  is the adsorption of a molecule, and  $v_0$  is the average thermal velocity of the molecules in the gas. We can thus find  $\tau_{\text{ads}}$  by measuring the photoionization signal  $U_{\text{srf}}$  corresponding to complete desorption of the molecules from the surface [this signal is proportional to  $n_{\text{srf}} (U_{\text{srf}} \propto n_{\text{srf}})$ ] and the photoionization signal from the UV illumination of the gas,  $U_{\text{gas}}$ , in the absence of the surface bombardment ( $U_{\text{gas}} \propto n_{\text{gas}}$ ). In the case of the naphthalene, measurements of the ratio  $U_{\text{srf}}/U_{\text{gas}}$  yield the value  $\tau_{\text{ads}} = 5 \times 10^{-3} \text{ s}$ , according to (3). From (1) we easily find the adsorption energy  $E$  of the naphthalene on the graphite:

$$E = kT \ln(\Omega \tau_{\text{ads}}) = 0.46 \text{ eV}. \quad (3)$$

Substituting in  $T = 200 \text{ K}$ , adopting  $\Omega = 10^{13} \text{ s}^{-1}$  as an estimate, and substituting the adsorption energy  $E$  into (2), we can determine the surface temperature corresponding to complete desorption of the molecules during the pulse from the CO<sub>2</sub> laser, of length  $\tau_p \approx 10^{-7} \text{ s}$  (the energy density of the CO<sub>2</sub> laser is 0.05–0.06 J/cm<sup>2</sup>):

$$T = E/k \ln(\Omega \tau_p) = 390 \text{ K}. \quad (5)$$

At  $E = 0.4 \text{ J/cm}^2$  (Fig. 1) the surface is thus heated to about 1700 K. This conclusion agrees with the observed emission from the substrate. This heating apparently causes a thermal decomposition of molecules, both molecules on the surface and molecules of the evaporated substrate material near the surface.

In summary, these experiments demonstrate that ultrathin films of molecules on a surface ( $10^{-8}$ – $10^{-10}$  of a monolayer) can be reliably detected through laser photoionization detection of molecules desorbed from the surface.

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