

Multiphoton Ionization of Ion-Beam and Laser Desorbed Molecules from Organic Surfaces

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Abstract. The time-of-flight (TOF) distributions of neutral molecules desorbed from a surface using a pulse of ions or photons have been measured using multiphoton ionization. Pyrenebutyric acid molecules sputtered from a thick layer of this material have kinetic energies centered around 0.1 eV. Molecules ejected from a thick layer of tryptophan undergo delayed ejection when either fast ions or photons (266 nm) initiate the desorption event.

INTRODUCTION

The low detection limits afforded by resonant multiphoton ionization provide an ideal way to study desorption processes initiated by energetic probes such as fast ions or photons. Ion beam and laser desorption are the basis behind a number of emerging techniques for organic and biological surface analysis, and understanding the details of molecular ejection has become increasingly important. Detection of sputtered neutrals by laser multiphoton ionization enables separation of the desorption and ionization processes and consequently provides information specific to the molecular ejection event. Time-of-flight (TOF) desorption profiles have been measured for molecules ejected from thick layers of pyrenebutyric acid and tryptophan using keV ions as the desorption probe. The desorption behavior of tryptophan was also investigated using 266 nm radiation.

EXPERIMENTAL

Ion-beam-induced desorption was achieved using 8 keV, 500 ns pulses of Ar⁺ focused to a 3 mm diameter spot on the surface. The 266 nm radiation used for

laser desorption was generated using the fourth harmonic of a Nd-YAG laser. Postionization of the desorbed neutral molecules was achieved using 280 nm (3 mJ/pulse) radiation produced from the frequency doubled output from a Nd-YAG pumped dye laser. TOF distributions were measured by systematically changing the delay between the probe pulse and ionization pulse. The distance from the surface to the ionizing laser beam was approximately 1 cm. The identity of the postionized species was determined using TOF mass spectrometry. Thick layers of pyrenebutyric acid and tryptophan were prepared as pellets.

RESULTS AND DISCUSSION

TOF distributions obtained for neutral tryptophan molecules desorbed using 8 keV Ar⁺ and 266 nm photons (10⁴ W/cm²) are shown in Figure 1. The profiles were recorded for postionized fragments appearing at m/z 130, 116, and 93. No molecular ion was present in the postionization mass spectrum and m/z 130 was found to be the most intense ion regardless of the desorption probe.

Several interesting features are present in these distributions. Unique to the m/z 130 profile generated using the Ar⁺ projectile is a rather well defined peak centered at approximately 35 μ s. Transformation of the peak to kinetic energy coordinates indicates that these molecules are ejected from the surface with translational energies on the order of 0.1 eV which is in the range expected for a molecular collision cascade.¹ This feature, which is attributed to ejection via a ballistic mechanism is not present in any of the other distributions.

A feature which is common to all of the profiles is a high TOF tail which shows that molecules or molecular fragments continuously desorb from the surface for up to 200 μ s after irradiation with ions or photons. Several important points should be noted. The remarkable similarity between the distributions obtained using ions and photons strongly suggests a common desorption mechanism. The fact that delayed desorption is observed indicates that the probe energy is not rapidly dissipated into the solid and is "stored" in a manner which facilitates ejection over an extended period of time. This is in sharp contrast to the behavior of metal surfaces under ion-beam bombardment where events leading to ejection cease approximately 200 fs after ion impact.²

Although 266 nm photons and fast ions produce similar TOF distributions for tryptophan, the individual fragment ions recorded have significantly different profiles. The broad profiles of m/z 130 and 116 show no significant reduction in intensity for up to 200 μ s after irradiation. In contrast, the intensity of m/z 93 decreases rapidly from 50 to 150 μ s. An observation which may be related to this behavior is that the ions at m/z 130 and 116 correspond to the entire amino acid side chain and the indole ring, respectively, and both may be formed by a direct bond cleavage process. However, m/z 93 does not appear to correspond to a

direct cleavage and is likely formed via rearrangement. It is presently unknown whether the detected fragments are emitted directly from the surface or are formed during the ionization process.

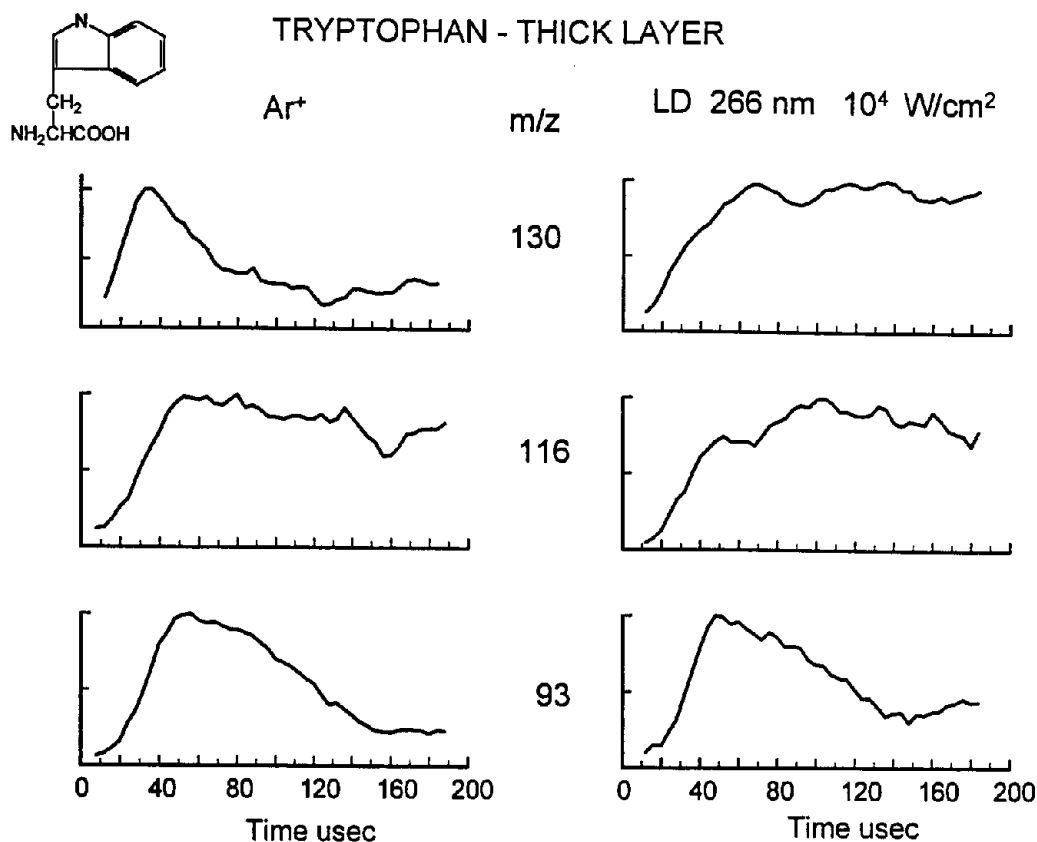


FIGURE 1. TOF profiles for fragments of tryptophan desorbed by 8 keV Ar⁺ and 266 nm photons.

While mechanistic interpretations are preliminary, two possibilities have been considered. One explanation for delayed ejection is surface heating. Organic solids are poor conductors and localized temperature spikes may persist for some time. This explanation is reasonable in the case of laser desorption in which the 3 mm surface spot is irradiated with 10^{13} photons/pulse. However, in the case of ion bombardment, the low ion dose (10^6 ions/pulse) means that desorption is initiated by single ion events and heating under these circumstances seems less likely. Another possibility is that surface irradiation may induce electronic transitions within the surface molecules. Tryptophan is known to have a long lived triplet state. If this state is populated by transitions initiated by 266 nm photons or fast ions, the energy released upon non-radiationless decay may account for the delayed ejection behavior. Further investigations are underway to explore these possibilities.

The TOF distribution for molecules ejected from a thick layer of pyrenebutyric acid upon 8 keV Ar⁺ bombardment is shown in Figure 2. This profile was obtained by recording the intensity of the molecular ion (m/z 288). The distribution obtained when recording a fragment at m/z 215 was nearly identical to that of that of the molecular ion which suggests that some fragmentation occurs during the ionization process. Transformation of this distribution to energy coordinates shows that molecules leave the surface with an average translational energy of 0.2 eV, implying a ballistic ejection mechanism. In contrast to tryptophan, no delayed ejection is evident for this system and no molecules are present in the laser plane 100 μs after the desorption pulse.

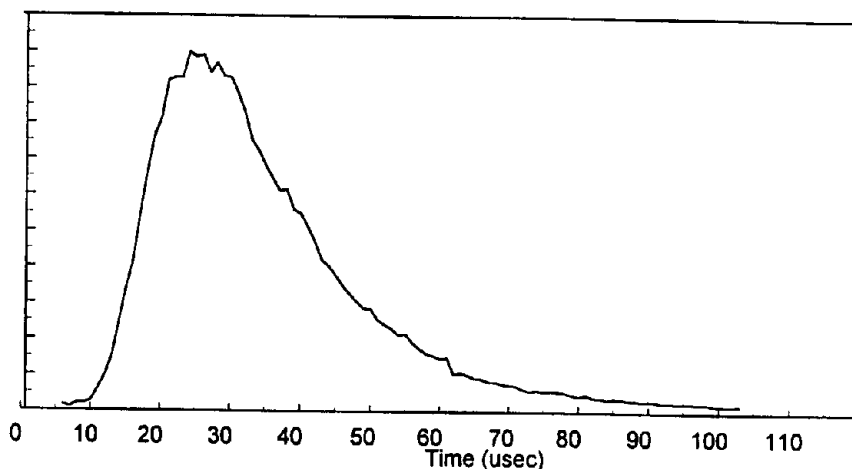


FIGURE 2. TOF distribution for pyrenebutyric acid desorbed by 8 keV Ar⁺ ions.

ACKNOWLEDGMENTS

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¹ Hoogerbrugge, R., van der Zande, W.J., Kistemaker, P.G, *Int. J. Mass Spectrom. Ion Processes.*, **76**, 239 (1987).

² Garrison, B.J., *Nucl. Instrum. Methods B*, **17**, 305 (1986).