RAPID COMMUNICATIONS IN MASS SPECTROMETRY
Rapid Commun. Mass Spectrom. **12**, 1226–1231 (1998)

Ejection of Neutral Molecules from Ion-bombarded Organic Surfaces

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Time-of-flight distributions of neutral molecules ejected from various organic surfaces have been measured subsequent to 8 keV Ar^+ and $H_2{}^+$ ion bombardment. The distributions show that depending on the physical and chemical nature of the substrate, the neutral molecules have strikingly different desorption profiles. For C_6H_6/Ag{111}, at low coverage the C_6H_6 molecules eject with energies in the range 0.25–1 eV while at high coverage most of the molecules desorb with thermal kinetic energies (~0.04 eV). At intermediate coverage two peaks are present in the time-of-flight distribution indicating that two different mechanisms contribute to the desorption process. For self-assembled monolayers of phenylethanethiol on Au, while a minor ejection is observed at higher kinetic energy (~1 eV) most of the molecules desorb with thermal kinetic energies (~0.03 eV). Pyrenebutyric acid molecules ejected from monolayer and multilayer samples have kinetic energies close to 0.2 eV. One ejection mechanism is observed in this case. For tryptophan, most molecules eject with kinetic energies close to 0.1 eV. In addition, a feature unique to this case is the continuous emission of molecules from the surface that extends beyond 200 μs after ion impact. For all the multilayer samples investigated, a molecular collision cascade in the solid leads to ejection of molecules with kinetic energies in the range 0.1–0.3 eV. © 1998 John Wiley & Sons, Ltd.

Received 24 April 1998; Revised 22 July 1998; Accepted 24 July 1998

Ion beam induced desorption techniques have found useful applications in molecular surface characterization of organic and biological systems.[1–5] Of fundamental interest is the interaction of ion beams with organic solids and the mechanisms that lead to molecular desorption. It is well known that a collision cascade leads to ejection of atomic species in the case of metals and semiconductors.[6,7] Various mechanisms have been put forth to describe the process by which the primary ion beam dissipates energy into the molecular solid to lead to the ejection of molecules.[8–13] These include sputtering via a collision cascade and momentum transfer,[14–17] various thermal desorption mechanisms[18,19] and mechanisms involving electronic processes.[20,21]

It is important to be able to isolate the contributions of the various mechanisms that lead to molecular desorption. The type of ejection mechanism proposed is generally determined by the behavior of the relative yields, kinetic energy and angular distribution of the ejected species. Most of the earlier studies have been performed on desorbed ions rather than neutral molecules. Interpretation of ion data is not straightforward since the nuclear motion is convoluted with the ionization process.

In the present study, time-of-flight and energy distributions of various neutral molecules ejected upon keV ion bombardment of different types of organic surfaces have been investigated. First, benzene/Ag{111} has been employed as the simplest molecular adsorbate. Benzene (C_6H_6) exposure was varied to obtain sub-monolayer to multilayer coverage on the Ag substrate. Next, self-assembled monolayers of phenylethanethiol on gold and pyrenebutyric acid (PBA) on Al were employed as more complicated systems where the molecule is bound to the surface by strong chemical bonds. And finally, we examined the behavior of multilayer samples of PBA on various substrates and solid biological materials such as tryptophan. Each of these systems exhibit very different behavior, depending on the physical and chemical nature of the system. From this complex behavior we can begin to propose a more general approach for predicting and understanding the desorption mechanisms of ion bombarded molecular films.

EXPERIMENTAL

The apparatus used to measure energy and angle resolved neutral (EARN) distributions has been described in detail elsewhere.[22] Briefly, the measurements were performed in an ultra high vacuum (UHV) chamber with a base pressure of 3×10^{-10} Torr. A desorption event is initiated by 8 keV $Ar^+/H_2{}^+$ ion pulse focused to a 3 mm diameter spot on the surface. A position sensitive microchannel plate (MCP) detector detects the ejected neutral species after multiphoton postionization with a 6 ns laser pulse. A 266 nm laser pulse obtained from a frequency quadrupled Nd-YAG laser is employed to non-resonantly ionize the neutral benzene and phenylethanethiol molecules. Tryptophan and pyrenebutyric acid molecules are ionized using 280 nm radiation

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Contract/grant sponsor: National Science Foundation.
Contract/grant sponsor: National Institutes of Health.
Contract/grant sponsor: Office of Naval Research.
Contract/grant sponsor: Polish Committee for Scientific Research.
Contract/grant sponsor: Maria Skłodowska-Curie Fund.

CCC 0951–4198/98/181226–06 $17.50

produced from the frequency doubled output of a Nd-YAG pumped dye laser. The time-of-flight (TOF) distributions of the neutral molecules are recorded by varying the delay between the ion pulse and the laser pulse. Energy distributions are obtained after coordinate transformation of the measured TOF distributions using the appropriate mass and surface to laser distance.[22]

The angle of incidence of the primary ion beam is 45° and the neutral molecules ejected normal to the surface are detected within an angular range of ±20°. The distributions are obtained after averaging 100 laser shots at each delay time. The measurements are made under static conditions and the primary ion dose is kept below 10^{12} ions/cm^2 in all experiments.

Sample preparation

Sub-monolayer to multilayer samples of C_6H_6/Ag{111} were prepared by condensing varying amounts of benzene vapor onto a clean Ag{111} crystal cooled to 120 K. The Ag{111} crystal was cleaned with alternate cycles of sputtering and annealing at 450 °C until sharp LEED spots were obtained. The gases dissolved in C_6H_6 were removed by several freeze–pump–thaw cycles before dosing. The benzene vapor was introduced into the UHV chamber using a leak valve. The C_6H_6 exposure was controlled by monitoring the chamber pressure and the dosing time. All exposures are reported in Langmuir units ($1\ L = 1 \times 10^{-6}$ Torr s) and are uncorrected for ion gauge sensitivity factor of 5.8.[23]

Self-assembled monolayers (SAM) of phenylethanethiol were prepared by immersing vapor deposited gold substrates in 30 mM solutions of phenylethanethiol in ethanol. The gold substrates were kept in the solution for at least five days and were then rinsed in ethanol before introduction into the UHV chamber.

The tryptophan sample was prepared by compressing the tryptophan powder in a KBr press to form a pellet of approximately 2 mm thickness.

Pyrenebutyric acid samples were prepared by spin coating 1 drop of a 23 mM solution of pyrenebutyric acid in acetone onto various substrates, i.e. vapor deposited Au and Al. The self-assembled monolayer films were prepared by immersing vapor deposited Al substrate into 1 mM solution of pyrenebutyric acid in acetone. The substrates were kept in solution for four days and were then rinsed in acetone.

RESULTS AND DISCUSSION

To unravel the various factors that may contribute to molecular ejection, we measured TOF distributions of neutral molecules after keV ion bombardment of different organic materials. The various samples investigated are, (a) C_6H_6/Ag{111}, where the measurements were performed for various C_6H_6 coverages ranging from a regime where the molecules exist in near isolation on the metal surface to where they are bound in multilayers of frozen C_6H_6, (b) self-assembled monolayers of phenylethanethiol on gold, where the thiol molecules form a chemical bond to Au, (c) pyrenebutyric acid self-assembled monolayer films on Al and multilayer films on Al and Au, and (d) solid samples of tryptophan.

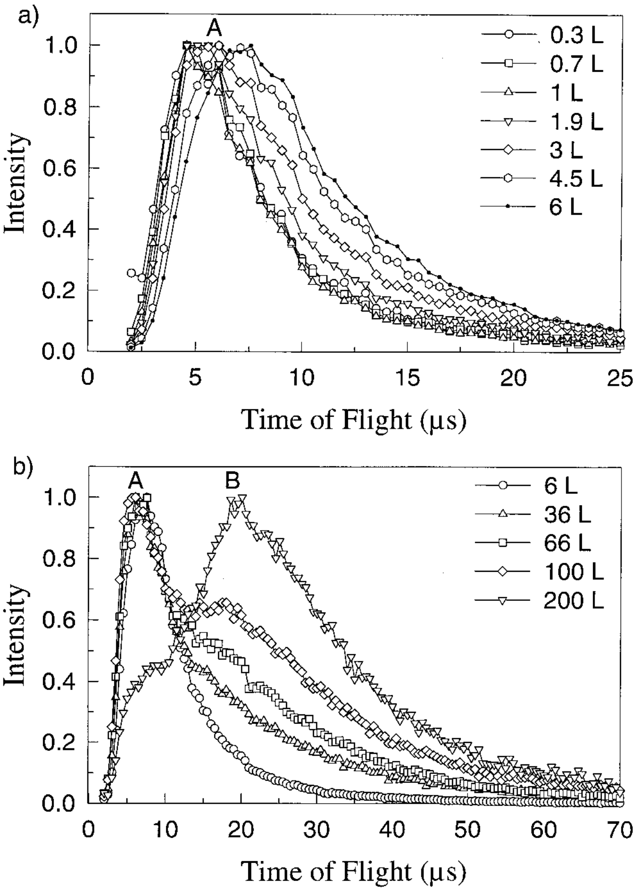

Figure 1. The time-of-flight distributions of neutral benzene molecules for (a) low exposures, (b) high exposures expressed in langmuirs (L). The high and low kinetic energy components are labeled A and B.

Sub-monolayer to multiyayer coverage of C_6H_6 on Ag{111}

The TOF distributions of neutral C_6H_6 molecules obtained after 8 keV Ar^+ ion bombardment of C_6H_6/Ag{111} for various C_6H_6 exposures are shown in Fig. 1. The distributions have strikingly different shapes depending on the exposure. At low exposures (Fig. 1(a)) a peak at short TOF (peak A) is present and for high exposures (Fig. 1(b)) another peak at long TOF (peak B) begins to dominate the distribution. The C_6H_6 distribution at 1 L is quite similar to that observed for desorbed silver atoms, suggesting that at low exposures collisions between the substrate particles and the adsorbed molecules lead to ejection of C_6H_6 molecules.

As shown in Fig. 1(b), C_6H_6 exposure above 6 L does not influence the position of peak A but rather results in an increase in signal intensity at a longer TOF (peak B). The intensity of peak A gradually decreases and peak B begins to dominate the TOF distribution. At intermediate coverage, both the peaks are present indicating that two different mechanisms contribute to the desorption process. At very high exposures (800 L) when peak A is absent in the TOF distribution, the mass spectrum has no Ag or Ag_2 signal characteristic of the substrate.

The molecules within peak B eject with extremely low kinetic energies with the peak energy being 0.04 eV. A thermal desorption mechanism could explain this low energy emission. As shown in Fig. 2 the TOF distributions for 800 L exposure do not change with surface temperature

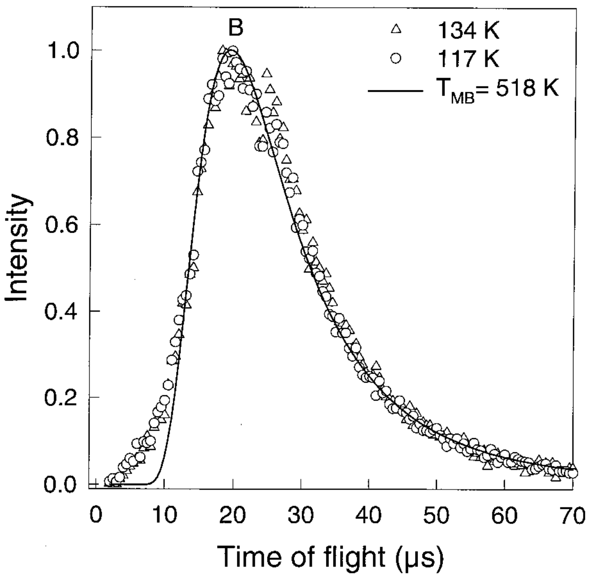

Figure 2. The time-of-flight distribution of neutral benzene molecules for 800 L exposure, at different surface temperatures. The solid line shows a Maxwell–Boltzmann distribution with a fit temperature of 518 K.

over the investigated temperature range (117 K–134 K). Although the TOF data could be fit to a Maxwell–Boltzmann distribution using a temperature parameter of 518 K, the fit temperature is much above the experimental surface temperatures.

These calculations show that for multilayer coverage the C_6H_6 molecules eject with effective thermal energies that are higher than the surface temperature. The ejection of C_6H_6 molecules is not observed with much the lighter H_2^+ projectile ions meaning that a momentum transfer process is crucial to this thermal emission. A molecular collision cascade can trigger vibrational and rotational excitation of the molecules and exothermic reactions of fragments formed in the cascade. This can cause local heating of the C_6H_6 multilayers and emission of molecules with effective temperatures higher than the macroscopic surface temperature. The low thermal conductivity of the benzene layer would prevent dissipation of heat and stimulate evaporation of the weakly bound C_6H_6 molecules.

Self-assembled monolayers of phenylethanethiol/Au

The TOF distributions of neutral phenylethanethiol fragment at *m/z* 105 obtained after 8 keV Ar^+ and H_2^+ ion bombardment of self-assembled monolayers of phenylethanethiol on gold ($C_6H_5CH_2CH_2S$-Au) are shown in Fig. 3(a). Distributions were recorded for *m/z* 105 ($C_6H_5CH_2CH_2$) because it was the most abundant peak in the mass spectrum. No molecular ion was observed in the postionization mass spectra obtained after sputtering or gas phase ionization of phenylethanethiol, indicating that the phenylethanethiol molecules photofragment in the laser plane.

The TOF distribution obtained with the Ar^+ projectile has two components, a low TOF peak A and a much more dominant high TOF peak B. Upon transformation to kinetic energy coordinates it is found that peaks A and B correspond to approximately 1 eV and 0.03 eV, respectively. Only peak B is observed when H_2^+ ion is used as the projectile. The desorption profile of peak A is quite similar to that of the sputtered gold, indicating that both the species leave the surface with the same velocity. This observation along with the fact that the peak A and signal from the gold substrate are absent during H_2^+ bombardment indicate that a momentum transfer from the gold substrate to the organic overlayer initiates the ejection of the molecules within peak A. These observations are similar to the ballistic ejection of benzene molecules (Fig. 1, peak A).

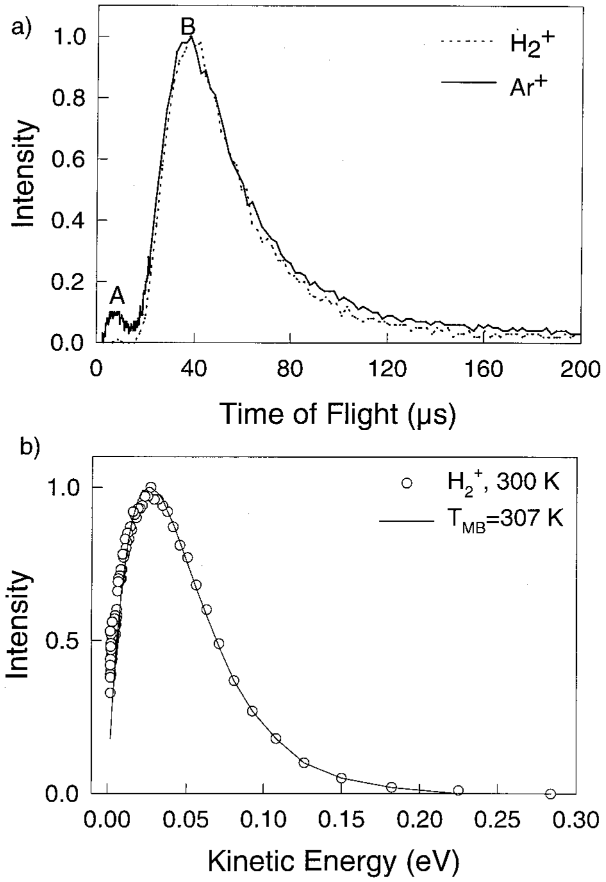

Figure 3. (a) The time-of-flight distributions of neutral phenylethanethiol fragment at *m/z* 105 obtained using 8 keV Ar^+ and H_2^+ projectiles. The high and low kinetic energy components are labeled A and B. (b) The kinetic energy distribution of the phenylethanethiol fragment emitted after 8 keV H_2^+ ion bombardment at 300K surface temperature shown with the corresponding Maxwell–Boltzmann fit.

The low energy component (peak B) being the most pronounced peak in the TOF distribution, is of particular interest. The shape of the profiles obtained using Ar^+ and H_2^+ projectiles are similar. The corresponding kinetic energy distribution for the H_2^+ projectile, as shown in Fig. 3(b), could be fit by a Maxwell–Boltzmann distribution at room temperature. Cooling the sample resulted in a marked shift in the distribution towards lower energies. The molecules leave the surface with very low kinetic energies with the peak energy being close to 0.03 eV. This is quite striking because the molecule is bound to the surface by a S–Au bond with an estimated bond energy of 2 eV. In our previous paper, we have shown that this low energy thermal emission can be explained by chemical reactions that result in bond cleavage.[24] Highly reactive species, such as $H^{\cdot}$, H^+ and H^-, created by the interaction of the primary beam with the organic film may react with intact molecules to sever the surface bond. These molecules can then evaporate from the surface. Bond cleavage by chemical reactions will be much gentler than direct bond scission and thus is more likely to form products which desorb with thermal kinetic energies.

It is interesting to note that the ejection of molecules from chemisorbed self-assembled monolayers of phenylethanethiol on gold and physisorbed monolayer films of C_6H_6 are quite different. For phenylethanethiol self-assembled monolayers, along with the minor ballistic ejection, desorption mainly occurs by a thermal mechanism. However for monolayer films of C_6H_6 only the ballistic mechanism leads to ejection.

It is also instructive to compare the desorption from phenylethanthiol self-assembled monolayers and C_6H_6 multilayer ice. The two systems are obviously quite different yet both exhibit thermal desorption. The phenylethanethiol molecules form a thin monolayer film on a metal substrate, while the C_6H_6 molecules are in a multilayer ice. Therefore the thermal conductivities of the two systems are very different. The self-assembled monolayers are bound to the gold surface by strong chemical bonds, while the C_6H_6 molecules are weakly bound by van der Waals interactions.

The desorption mechanism though thermal in character is also quite different for the two systems. First, though both display Maxwell–Boltzmann distribution, the fit temperature tracks the surface temperatures for the thiol while the fit temperatures are higher than the surface temperature for benzene. Second, desorption is initiated by H_2^+ ions for the thiol but not for C_6H_6. Third, the TOF distributions of the thiol are strongly dependent upon the surface temperature whereas that of C_6H_6 do not change significantly over the investigated temperature range. Finally, we propose that the thermal desorption of phenlyethanethiol molecules involves bond cleavage by chemical reactions and eventual evaporation while desorption of C_6H_6 molecules arise from local heating of the substrate.

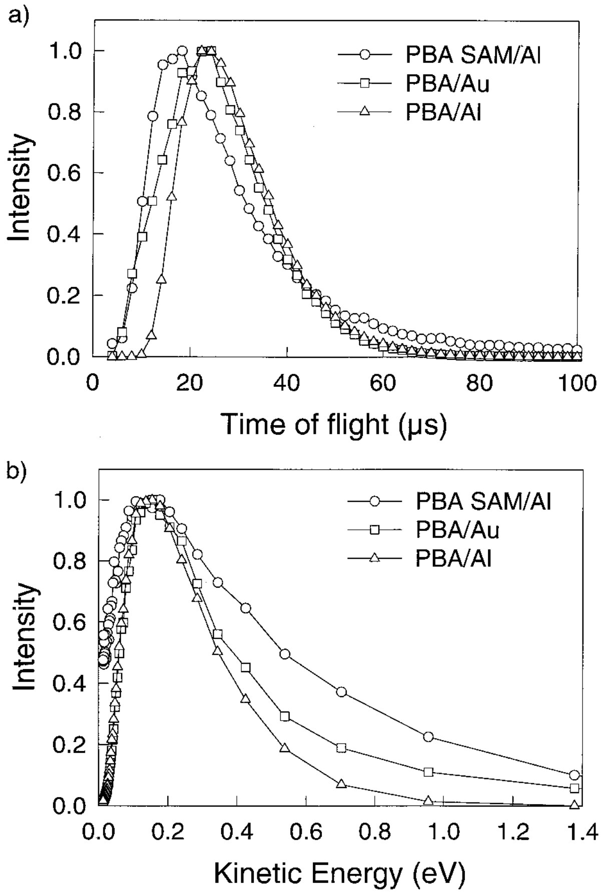

Figure 4. The (a) time-of-flight distributions and (b) kinetic energy distributions of neutral PBA fragment (*m/z* 215) ejected from self-assembled monolayer of PBA on Al (PBA SAM/Al), and multilayer films of PBA on Au and Al substrates (PBA/Au and PBA/Al).

Pyrenebutyric acid films on various substrates

The TOF distributions of pyrenebutyric acid (PBA) fragment at *m/z* 215 obtained after 8 keV Ar^+ ion bombardment of self-assembled monolayer films of PBA on Al and multilayer films of PBA on Au and Al are shown in Fig. 4(a). The fragment at *m/z* 215 is the most intense peak in the postionization mass spectrum. The TOF distribution of the fragment is nearly identical to that of the molecular ion suggesting that most of the fragment molecules are formed by photofragmentation of the PBA molecules in the laser plane. The TOF distributions were recorded for the fragment to achieve better signal to noise ratio.

Unlike the earlier systems studied, all the TOF distributions in this case have one well-defined peak. The distribution shifts towards longer TOF for the lighter substrate. Also, by comparing the monolayer and multilayer samples on Al it is evident that the TOF shifts to a lower value for the monolayer sample.

The kinetic energy distributions for the various PBA samples are shown in Fig. 4(b). In all the cases the molecules eject with peak energies close to 0.2 eV. The distributions however depend on the mass of the substrate and the thickness of the overlayer. The tail of the kinetic energy distribution shows that for the Al substrates, molecules eject with higher energies from the monolayer sample as compared to the multilayer sample. This trend is consistent with the ejection of C_6H_6 molecules within peak A. In the case of the multilayer films, the PBA molecules eject with higher energies from the heavier Au substrate as compared to the lighter Al substrate. These observations indicate that a ballistic mechanism is responsible for the ejection of PBA molecules.

Of note is the fact that the TOF distribution of self-assembled monolayers of PBA on Al does not have any thermal component similar to that observed for SAMs of phenylethanethiol on Au. This is not unexpected because the bond cleavage for the thiol self-assembled monolayers is proposed to occur due to chemical reactions. Such a mechanism should be specific to the functional group of the molecule binding to the surface and therefore the bond cleavage and thermal desorption is unique to the thiol monolayer.

Also interesting to note is that the ejection of PBA molecules occurs with kinetic energies similar to the C_6H_6 molecules emitted from monolayer and intermediate multilayer coverages. The ejection of molecules from physisorbed monolayer films of C_6H_6 and chemisorbed self-assembled monolayers of pyrenebutyric acid occurs with similar kinetic energies. The emission of molecules from multilayer films presents a striking contrast in the two cases. For C_6H_6 at intermediate coverage, along with the ballistic process described above, desorption also occurs by a thermal mechanism. This is quite different for pyrenebutyric acid molecules where ejection from monolayer as well as multilayer films occurs at the same kinetic energy. A single ejection mechanism described by the molecular collision

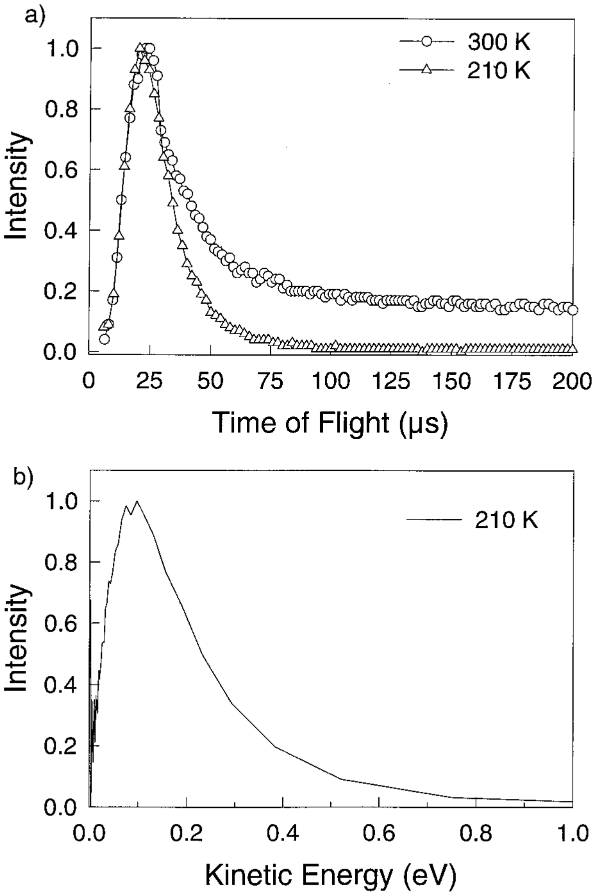

Figure 5. (a) The time-of-flight distributions of neutral tryptophan fragment at *m/z* 130 measured at different surface temperatures. (b) The kinetic energy distribution of the tryptophan fragment at 210 K surface temperature.

cascade leads to ejection of pyrenebutyric acid molecules for all the different overlayer/substrate combinations investigated.

Solid tryptophan

The TOF distributions of neutral tryptophan fragment at *m/z* 130 obtained after 8 keV Ar^+ ion bombardment of a tryptophan pellet at 300 K and 210 K surface temperatures are shown in Fig. 5(a). No molecular ion was present in the postionization mass spectrum and the peak at *m/z* 130 was found to be the most intense.

The TOF distributions at both the surface temperatures have a well-defined peak close to 20 μs. A unique feature in the TOF distribution at 300 K is the continuous emission of molecules or molecular fragments that lasts longer than 200 μs after ion bombardment. This delayed emission indicates that the probe energy is not directly dissipated into the solid but is rather stored in a manner which facilitates ejection over an extended period of time. This emission is not found at 210 K, indicating that either the storage of energy is temperature dependent or the delayed emission gets quenched at lower temperatures. A possible explanation may be that the primary ion induces electronic transitions within the surface molecules. Tryptophan has a long lived triplet state which, if populated by transitions induced by fast ions, may cause energy release after radiationless decay and account for the delayed emission. Transitions to the triplet state should also be induced by photons. We have indeed observed similar long emission times, when tryptophan is irradiated with 266 nm photons.[25]

The kinetic energy distribution obtained after coordinate transformation of the TOF distribution at 210 K is shown in Fig. 5(b). The peak in the energy distribution is close to 0.1 eV. The molecules eject with kinetic energies similar to that of C_6H_6 and pyrenebutyric acid molecules. We postulate that a molecular collision cascade in the typtophan solid leads to ejection of molecules with kinetic energies close to 0.1 eV. Coordinate transformation of the TOF distribution at 300 K would not be appropriate because the ballistic peak is convoluted with long emission times. It is therefore difficult to estimate the kinetic energies with which the molecules desorb in the delayed emission process.

CONCLUSION

We have examined the time-of-flight and kinetic energy distributions of neutral molecules ejected from various organic surfaces by energetic ion bombardment. The results present a complex mechanistic picture indicating that more than one mechanism contributes to the ejection of molecules from organic solids. The desorption profiles of the molecules are strikingly different depending on the physical and chemical nature of the molecule/substrate complex. For C_6H_6/Ag{111}, at low coverage the molecules eject due to collisions with substrate particles whereas at high coverage the desorption has more of a thermal nature. At intermediate coverages, two peaks are present in the distributions suggesting that both the mechansims occur simultaneously during the desorption process. For self-assembled monolayers of phenylethanethiol on gold, while a minor ejection occurs due to collisions from the substrate particles, most molecules desorb with very low kinetic energies. The velocity distributions fit to the Maxwell–Boltzmann equation with temperature values close to the surface temperature. For pyrenebutyric acid films a ballistic mechanism is responsible for ejection from monolayer and multilayer films. For solid tryptophan samples, though most molecules eject due to a ballistic process, emission of molecules that extend to long times after ion impact is observed at room temperature. Finally, is it possible to form a unified picture of molecular desorption from this complex puzzle? In all the multilayer systems investigated the molecular collision cascade within the solid results in ejection of molecules with kinetic energies in the range 0.1–0.3 eV. We can begin to propose a more general approach to predict and understand the desorption mechanisms of ion-bombarded molecular films. Developing a theory for the molecular collision cascade will be important in achieving this goal.

Acknowledgements

We acknowledge the financial support of the National Science Foundation, the National Institutes of Health, the Office of Naval Research and the Polish Committee for Scientific Research and Maria Skłodowska-Curie Fund. We thank Tim Dunbar for his assistance in the preparation of the self-assembled monolayer films.

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