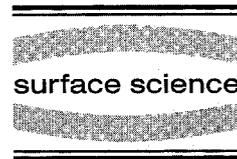




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## Erratum

# Erratum to: “ToF-SIMS analyses of polystyrene and dibenzanthracene: Evidence of the fragmentation and metastable decay processes in the molecular secondary ion emission” [Surf. Sci. 381 (1997) 18]<sup>1</sup>

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It has been assumed in our article that the secondary ion intensity corresponding to a negative apparent energy in the kinetic energy spectra of Figs. 8, 9, 12 and 13 were due to the fragmentation of metastable secondary ions *in the acceleration section of the spectrometer*. Although this interpretation accounts for the smooth exponential decay directed towards negative energies, our very recent experiments have shown that the intensity observed for a negative apparent energy is not only due to unimolecular dissociation in this part of the spectrometer.

Using a different value of the nominal extraction voltage (4.4 keV instead of 3 keV), we were able to verify unambiguously that the well-defined, gaussian peaks were actually due to metastable decay reactions occurring *in the field free drift region of the spectrometer*, between the acceleration section and the first hemispherical electrostatic analyzer. For a given ion, the increase of the extraction voltage corresponds to a reduction of the time

spent in the acceleration section. In the case of  $C_{22}H_{14}^+$  sputtered from dibenzanthracene, the calculated decay time distribution for the loss of H and  $H_2$  peaked at  $1.5 \times 10^{-7}$  s assuming our first hypothesis. In comparison, the total time spent in the acceleration section for a stable  $C_{22}H_{14}^+$  is  $1.75 \times 10^{-7}$  s with the 3 kV acceleration voltage. Increasing the acceleration voltage to 4.4 kV reduces this time to  $1.40 \times 10^{-7}$  s, which is less than the proposed decay time. If our first hypothesis was right, with the 4.4 kV voltage, most of the metastable  $C_{22}H_{14}^+$  would undergo fragmentation in the Einzel lens or in the drift region following the acceleration section. This would result in a partial or complete loss of the well-defined metastable peaks or, at least, in a severe modification of their shape (narrowing of the peak). Instead of this, with increasing extraction voltage, we observed only an increase of the energy shifts of the metastable peaks by a factor close to 1.5, corresponding exactly to the increase of the extraction voltage, but no modification of the peaks shapes and intensities. Moreover, the decay time distribution calculated with Eqs. (3) and (4) for the new voltage would be centered around  $1.2 \times 10^{-7}$  s, which is not consis-

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tent with the  $1.5 \times 10^{-7}$  s calculated before. This shows, a contrario, that the metastable decay reactions giving rise to the well-defined gaussian peaks occur in the field free drift region.

In addition, our corrected interpretation is much more in agreement with the theory of unimolecular reactions [1], which predicts a distribution of surviving parents  $Y_p(t) = Y^0 \exp(-rt)$ , where  $r$  is the rate of dissociation. Thus, the distribution of delayed formation times of the daughter ions has the form  $Y_d = r Y^0 \exp(-rt)$ , which is far from the nearly gaussian curves calculated in Fig. 11.

In our new interpretation: (i) if dissociation occurs in the acceleration section of the spectrometer, the exponential decay of the metastable parent ion intensities with time will account for the exponential decay of the intensities in the daughter ion energy spectra, because the kinetic energy lost is a square function of time in this section; (ii) in contrast, if dissociation occurs in the field free drift region of the spectrometer, it will be observed as a narrow, well-defined peak, because the energy deficit is no longer time-dependent in this section. The slight broadening of the peaks and the increase of this broadening with the mass of the neutral lost (Fig. 9) are explained by the angular momentum given to the daughter ions when the parents dissociate.

Consequently, Eqs. (3) and (4), valid in the

acceleration section, cannot be used to calculate the metastable lifetimes (Fig. 11) of the ions decaying in the drift region of the spectrometer. For the molecular ions considered in our paper, the time spent in the drift section is in the range  $10^{-7}$ – $10^{-5}$  s, which gives a rough estimation of the lower and upper limits of the actual formation times of the daughter ions produced in this region.

In addition, Eq. (5) must be replaced by the following relation (Eq. (5')), which allows an even more quantitative fit of the energy shifts in Figs. 8, 9, 12 and 13:

$$\frac{\Delta K}{K} \frac{m}{\Delta m} = 1. \quad (5')$$

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### References

- [1] W. Forst, *Theory of Unimolecular Reactions*, Academic Press, New York, 1973.