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THE ROLES OF ELECTRONIC AND NUCLEAR STOPPING IN THE
DESORPTION VALINE NEGATIVE MOLECULAR IONS*

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THE ROLES OF ELECTRONIC AND NUCLEAR STOPPING IN THE DESORPTION OF VALINE NEGATIVE MOLECULAR IONS*

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Résumé

Abstract - The yield of valine negative molecular ions has been measured as a function of Xe^+ , Kr^+ , and Ar^+ primary ion velocity. The electronic and nuclear stopping powers are comparable in magnitude and opposite in slope in the experimental velocity region. The yield data are explained in terms of electronic stopping power alone, with no contribution from nuclear stopping power within the experimental error. Low molecular weight atomic species are found to be best described by a nuclear stopping power related process.

Surfaces bombarded by energetic particles emit ionized and neutral species. This effect has been successfully exploited to obtain mass spectra of involatile organic compounds /1/. The bombarding particles are typically in either the 10 keV or in the 100 MeV energy range. Examples of these are alkali metal beams (keV), used in fast atom bombardment (FAB) and secondary ion mass spectrometry (SIMS), and fission fragments from ^{252}Cf (MeV), used in ^{252}Cf -plasma desorption mass spectrometry (PDMS). Although the mass spectra generated by incident ions in these two energy ranges are qualitatively similar /2,3/, the way in which the incident ions lose their energy to the sample are notably different. The electronic stopping power, $(dE/dx)_e$, is the dominant mode of energy loss in PDMS, while the nuclear stopping power, $(dE/dx)_n$, dominates in FAB and SIMS.

At high velocities ($v > v_0$), $(dE/dx)_e$ has been shown to be an important parameter in the desorption process of organic species /4-10/. The results are not clear for low velocity projectiles. Albers et al. /11/ have shown yield data suggesting that $(dE/dx)_n$ is more efficient than $(dE/dx)_e$ in the desorption of valine positive ions. Standing /12/ and Ens /13/ have measured the positive secondary ion yield of alanine as a function of incident alkali metal ion energy (1-16 keV). They conclude that $(dE/dx)_n$ is the predominant process, although they suggest that $(dE/dx)_e$ may also play a role in desorption. In a theoretical approach, Falcone et al. /14/ has concluded that desorption of secondary organic molecular ions is not likely to occur as a result of the nuclear

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collisional cascade associated with $(dE/dx)_n$.

In order to assess the relative roles of $(dE/dx)_n$ and $(dE/dx)_e$ we have measured the yield of valine negative molecular ions as a function of the velocity of noble gas ions in the region where $(dE/dx)_n$ and $(dE/dx)_e$ are comparable in magnitude and where $(dE/dx)_n$ is decreasing and $(dE/dx)_e$ is increasing.

The experimental apparatus, based on a time-of-flight analyzer, has been previously described in detail /15,16/. The primary Xe^+ , Kr^+ , and Ar^+ beams are produced and accelerated in the energy range 400 keV to 3.5 MeV using the 4.5-MV Dynamitron accelerator at Argonne National Laboratory. Typical incident ion count rates at the sample are $1000-3000\ s^{-1}$. The yield is defined as the number of secondary ions of interest per incident ion. The sample, the amino acid valine ($C_5H_{11}NO_2$) (MW=117), was prepared by electrospraying a $5\mu g/\mu l$ acetic acid:trifluoroacetic acid (4:1 by volume) solution.

Fig. 1 shows the negative valine molecular ion yield as a function of the velocity of Xe^+ , Kr^+ , and Ar^+ incident ions.

Fig. 1 - The yield of valine negative molecular ions as a function of incident ion velocity. The curves are yield functions based on $Y = K \cdot (dE/dx)_e^2$.

We observe that the $(M-II)^-$ yield increases with increasing velocity. The curves are fits to the data points based a constant, K , times the square of the electronic stopping power. This empirical square dependence has been observed and reported by many workers in this field /4-10,15,16/. The electronic stopping powers are calculated for valine from the Linhard-Scharff formulation /17/. We observe that the squared function of electronic stopping power describes the data well. The relative K values corresponding to Xe^+ , Kr^+ , and Ar^+ incident ions are 1.00, 0.66, 0.91.

Fig. 2 shows the negative valine molecular ion yield as a function of the velocity of Xe^+ incident ions as well as the calculated curves for $(dE/dx)_n$, $(dE/dx)_e$, and $(dE/dx)_{\text{total}}$ for Xe^+ ions in valine.

Fig. 2 - The yield of valine negative molecular ions as a function of the velocity of Xe^+ incident ions. The curves are the calculated stopping powers. The curve through the data points is a least squares fit based on $Y = K \cdot (dE/dx)_e^n$.

We have used average potential formulation of Wilson et al. /18/ with Bragg's rule to calculate the nuclear stopping power for valine. For calculation of the electronic stopping power in the velocity range of this experiment we have used the Linhard and Scharff formulation /17/. The total stopping power curve is simply the added Linhard-Scharff electronic and Wilson nuclear stopping powers. We observe that the neither the nuclear or the total stopping power describes the data points. The curve through the data points is a least squares fit based on an empirical relation :

$$\text{Yield} = K \cdot (dE/dx)_e^n$$

where K and n are empirically determined. The least squares n -value determined for Xe^+ incident ions is 1.6. Although the nuclear and electronic stopping powers of Xe^+ in valine are comparable in magnitude, the contribution from the nuclear stopping power is negligible within our experimental error of ~5%. Therefore, we expect that the energy loss associated with nuclear stopping is dissipated in some channel other than in desorption of valine negative molecular ions. Data for Kr^+ ($n=2.1$) and Ar^+ ($n=1.9$) incident ions also indicate minimal participation of their nuclear stopping powers in the desorption of valine negative molecular ions.

Fig. 3 shows the yield of low molecular weight secondary ions as a function of primary Xe^+ velocity.

Fig. 3 - The yield of low molecular weight ions from valine sample as a function of the velocity of Xe^+ incident ions.

We observe that the trend of the yield curves for C^- , CH^- , O^- , OH^- , and F^- follows nuclear stopping power curve, i.e., decreasing with increasing velocity. These results indicate that nuclear stopping plays a dominate role in the desorption process in a form suggestive of classical sputtering. However, like the more complex valine negative molecular ions, the CN^- and C_2H^- ion yield curves follow the electronic stopping power relation.

We have shown that the desorption of valine negative molecular ions can be related to the electronic stopping power alone, with no contribution from the nuclear stopping within our experimental error of $\sim 5\%$. These findings are in contrast to those of Albers et al. /11/, who found that for positive valine molecular ions, the nuclear stopping was the predominant process. The possibility that negative and positive ions arise from completely different mechanisms cannot be excluded. We have further shown that the low mass atomic and simple polyatomic negative ions are directly related to the nuclear stopping power, while more complex polyatomic ions are related to the electronic stopping power.

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