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SECONDARY ELECTRON EMISSION BY LOW ENERGY ION IMPACT

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Résumé

L'efficacité de détection des ions ayant des énergies dans le domaine du keV a été estimée en mesurant le nombre d'électrons émis sous impact à partir de surfaces métalliques recouvertes de Al₂O₃ et CsI. Les électrons secondaires étaient accélérés à 21 kV et leurs trajectoires courbées par un champ magnétique afin qu'ils puissent être détectés par un détecteur semi-conducteur refroidi. Une analyse de la forme des amplitudes des impulsions recueillies a été faite par ordinateur. On trouve que le nombre d'électrons émis de CsI est 10 fois plus grand que le nombre émis de Al₂O₃. La masse organique de 2000 u (gramecidine) produit par impact sur CsI environ 40 électrons et l'efficacité de détection est donc de 100 %. Il est aussi possible par cette méthode de distinguer un impact unique de plusieurs impacts simultanés par la détermination du nombre d'électrons émis.

Abstract

In order to estimate the detection efficiency of ion detectors in the keV regime, the secondary electron yield of metal plates covered by Al₂O₃ and CsI was measured using a ²³²Cf time-of-flight technique. The mono- and multiatomic ions were produced by ²³²Cf fission fragment impact on various solid samples and then accelerated by a 21 kV potential towards the metal plate. The secondary electrons ejected from the surface were directed by means of magnetic deflection to a cooled semiconductor detector having a resolution of 6.5 keV at 19 keV electron energy.

To deduce the mean number of electrons per impact the pulse height spectrum was defolded with help of a new computer supported formalism. In most cases the spectra could be defolded without a residual background - even at high electron yields, where the events of adjacent electron numbers were not resolvable. It was found that at 21 keV ion energy the number of electrons ejected from CsI is about one order of magnitude higher than that of Al₂O₃. The Gramecidine (M+1) ion produces about 40 electrons at CsI, that means, at least up to mass 2000 amu the detection efficiency was close to 100 %. It was possible to distinguish between one and two simultaneously detected ions of same mass. The relative electron yields plotted versus ion mass were compared with theoretical predictions. In case of multiatomic ions the electron yields are hardly explainable by the sum rule.

Introduction

In fast heavy ion induced desorption of secondary ions especially of organic samples the detection of very heavy molecular ions is of increasing interest.

The detection of those ions generally occurs over the secondary process of electron emission during the interaction with ion-electron conversion materials. In order to obtain a high detection efficiency it is necessary to use materials with high secondary electron coefficients. Since the emission of secondary electrons is mainly a kinetic process with a threshold velocity at least for monatomic ions [1] the detection of heavy molecular ions with velocities below this threshold is not obvious. The results of this study suggest a lowered threshold for the secondary electron emission in the case of the Gramecidine ion with a velocity of 4 \cdot 10^6 \text{ cm/s}. The estimation of real ion yields in the field of mass spectrometry needs informations about the detection efficiency as a function of particle mass and composition even

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in the case of heavy biomolecular ions, consisting of hundreds of atoms. Till now only a few attempts were made to estimate detection efficiencies of those ions [2]. It is shown that the often reported sum rule of secondary electron yields for metalls [3] fails in the case of insulators as conversion materials used in this work. For heavy molecular ions the observed electron yields are always smaller than the sum of the yields of the single atoms at the same velocity.

The suggested frequency distribution of the secondary electrons is a polya distribution [1], assuming that the emission from a very thin layer may be described by a poisson distribution and that contributions from deeper layers result in a broadening of the observed frequency distribution [4].

It was the purpose of this work to estimate the detection efficiency for molecular ions and to investigate the dependence of secondary electron yields from Al₂O₃- and CsI-surfaces on mass and composition of those ions.

**Experimental**

The principle of the ion-electron converter to obtain the frequency distribution of secondary electrons used in this study is depicted in fig.1. Positive secondary ions produced during bombardment of appropriate samples with ²³⁵U fission fragments were post accelerated by 19 kV up to a kinetic energy of 21 keV before striking the conversion electrode. The mass determination of the secondary ions was done by usual time of flight measurements. Secondary electrons ejected from the conversion electrode were accelerated by the 19 kV electric field and focused by a magnetic field onto a surface barrier detector. The magnetic field was generated by electro magnets placed outside the vacuum chamber. The cooled silicon surface barrier detector had an energy resolution of 6.5 keV with an active area of 100 mm². The signal of the surface barrier detector was used to define the energy of the secondary electrons and to produce the stop signal for the time-of-flight measurement.

Since the kinetic energy of the electrons is higher than the resolution for one electron one obtains clearly separated peaks belonging to different numbers of secondary electrons produced by the ion impact. Examples of energy spectra of secondary electrons are shown in fig. 2 for Cs⁺ respectively Valine (M+1)⁺ hitting the Al₂O₃-electrode.
The conversion electrode was a polished aluminium plate, assumed to be covered with 5-20 Å Al₂O₃ as a result of contact with air. In the second part of this study the electrode was vacuum evaporated with 4000 Å CaI. At a pressure of 10⁻⁶ torr impurities due to gas adsorption were not avoidable.

The acceleration grid had a transmission of 83% and a thickness of wires of about 25 μm. The yields of secondary electrons are corrected for possible absorption in the grid. Results of trajectory calculations suggest that losses of electrons due to other effects, like bad focusing, are negligible.

![Figure 2: Two examples of pulse height distributions obtained with the Al₂O₃-electrode. The ion energy is 21 keV.](image)

Pulse height and frequency distributions

The obtained energy spectra must be defolded in order to estimate the real frequency distribution of the secondary electrons. The simple way of deconvolution with ordinary Gaussian peaks gives only a bad agreement with pulse height distributions due to the low energy tail of the single electron peaks caused by backscattered electrons [5]. The sometimes used Lorenz peaks are also only an unsatisfying approximation. In the following part an attempt to improve the deconvolution taking backscattering of electrons into account is described. The pulse height distribution $H(h)$ of the surface barrier detector is related to the real energy spectrum $S(\epsilon)$ of the electrons by the equation

$$H(h) = \int_0^\infty S(\epsilon) \cdot R(\epsilon, h) \, d\epsilon. \quad (1)$$

$R(\epsilon, h)$ is the response function of the detector, and $R(\epsilon, h) \cdot dh$ is equal to the probability that an electron with an energy $\epsilon$ produces a pulse height between $h$ and $h + dh$. In our case $\epsilon$ shall be equal to 1 for an electron energy of 19 keV, equal to 2 for 38 keV etc. The response function itself is a folding of the noise distribution $G(E, h)$ of the detector with a function $D(\epsilon,E)$, which describes the distribution of deposited energy $E$ in the detector.

$$R(\epsilon, h) = \int_0^\epsilon D(\epsilon, E) \cdot G(E, h) \, dE \quad (2)$$

$D(\epsilon,E) \cdot dE$ is the probability that an electron of energy $\epsilon$ (an electron of 19 keV has $\epsilon = 1$) deposits an energy between $E$ and $E + dE$ in the detector. The real energy spectrum of the electrons is given by

$$S(\epsilon) = \sum_{N=1}^{\infty} w_N \cdot \delta(\epsilon - N). \quad (3)$$

The factors $w_N$ represent the frequency distribution of the emitted secondary electrons. These quantities have to be estimated. Inserting equation (3) into equation (1) one obtains after integration

$$H(h) = \sum_{N=1}^{\infty} w_N \cdot R(N, h). \quad (4)$$

$R(N,h)$ is the response function of $N$ electrons impacting the detector simultaneously.

When an electron hits the detector two possible destinies have to be distinguished. Either the electron is absorbed or it is backscattered. In the first case the total kinetic energy of the electron is deposited in the detector, in the second case the electron is backscattered and only a fraction of
its energy is deposited, which is assumed to be equally distributed between $E=0$ and $E=l$ \[6\]. The energy deposition distribution for one electron is therefore

$$D(1,E) = p \cdot D_E(1,E) + q \cdot \delta(E - 1)$$

$$D_E(1,E) = \begin{cases} 
1 & \text{for } 0 < E < 1 \\
0 & \text{else} 
\end{cases} \tag{5}$$

$p$: backscatter probability and $q = 1 - p$.

$D(1,E) \cdot dE$ is the probability that one single electron deposits an energy between $E$ and $E + dE$ in the detector. The distribution of the deposited energy $E = \sum E_i$ for two or more electrons impacting the detector is in the case of independent electrons a folding over the individual distributions.

$$D(2,E) = \int_0^E D(1,x) \cdot D(1,E-x) dx$$

$$D(N,E) = \int_0^{N-1} D(N-1,x) \cdot D(1,E-x) dx \tag{6}$$

with $D(1,E)$ of equation (5)

The solution of these equations leads to the energy deposition distribution of $N$ electrons.

$$D(N,E) = q^N \cdot \delta(E - N) + \sum_{n=1}^{N} \binom{N}{n} p^n q^{N-n} \cdot D_E(n,E-(N-n))$$

with

$$D_E(1,E) = \begin{cases} 
1 & \text{for } 0 < E < 1 \\
0 & \text{else} 
\end{cases}$$

$$D_E(2,E) = \begin{cases} 
E & \text{for } 0 < E < 1 \\
2 - E & \text{for } 1 < E < 2 \\
0 & \text{else} 
\end{cases}$$

$$D_E(n,E) = \frac{1}{\sqrt{2\pi\sigma_n^2}} e^{-\frac{(x-E)^2}{2\sigma_n^2}}$$

with $\sigma_n^2 = \frac{n}{12}$ for $n \geq 3$

One obtains the searched response function by inserting equation (7) into equation (2) with an appropriate noise distribution $G(E,h)$ given by.

$$G(E,h) = \frac{1}{\sqrt{2\pi\sigma_R^2}} e^{-\frac{(E-h)^2}{2\sigma_R^2}} \tag{8}$$

The noise function is estimated by reasonable values for the variance $\sigma_R^2$. A thermal and a statistical contribution due to the fluctuations of electron hole generation in the detector are considered.

$$\sigma_R^2 = \sigma_n^2 + N \cdot \sigma_3^2 \tag{9}$$

An analytic calculation of equation (2) for the response function is not possible. Since the variances of the distributions $D_E(N,E)$ are high compared with $\sigma_R^2$ the integration was performed only over the $\delta$-function and the rectangular distribution $D_E(1,E)$. This is important, because otherwise the final fit function is not continuous. Integration over the $\delta$-function leads to the noise distribution itself and the integration over the rectangular distribution is approximated by a sum of two Fermi functions with an adequate choice of the free parameters. The final response function for $N$ electrons was therefore calculated as

$$R(N,h) = q^N \cdot G(N,h) + \sum_{n=1}^{N} \binom{N}{n} p^n q^{N-n} \cdot R_E(n,h-(N-n))$$
The observed pulse height distribution should be well fitted for appropriate and reasonable values of the free parameters \( p, \sigma_S, \sigma_T, \sigma_F \) by the function

\[
H(h) = \sum_{N=1}^{\infty} w_N \cdot R(N, h).
\]

This equation was used as fit function. The parameter \( \sigma_F \) was not crucial and set as \( \sigma_F = \sigma_T \). For the other parameters mean values resulting from several fits were used:

- backscatter probability : \( p = 0.23 \pm 0.03 \)
- thermal contribution to \( \sigma_R \) : \( \sigma_T = 0.14 \pm 0.01 \)
- statistical contribution to \( \sigma_R \) : \( \sigma_S = 0.03 \pm 0.01 \)

(values of variances in units of 19 keV)

The backscatter probability is in good agreement with expected values [7], and the variances indicates an energy resolution of 6.5 keV. In the further calculations only the frequencies \( w_N \) were used as fit parameters delivering directly the frequency distribution of the secondary electrons.
Results and discussion

Al₂O₃-electrode

Absolute electron yields obtained with the Al₂O₃-electrode of the alkali-ions are shown in fig. 5 as function of ion mass. Similar results of relative electron yields for monoatomic ions have been reported by many other authors [8], [9], and even the maximum for Potassium is in good agreement with them.

In addition the relative behaviour is well describable by the model of Beuhler and Friedman [10] who assumed that

$$\gamma = k \cdot \int_0^\infty \frac{dE}{dx}_e \cdot e^{-\frac{x}{L}} \, dx. \quad (12)$$

$L$ is the diffusion length of internal secondary electrons. The integration is performed over the ion path length. The values for $(\frac{dE}{dx})_e$ were taken from Lindhard and Scharff [11] stopping power theory.

![Figure 4: Example of a fit adjusted with equation (11) to a pulse height spectrum from a CNH₄⁺ (Glycine-COOH) ion impinging on Al₂O₃.](image)

![Figure 5: Average electron yield $\langle \gamma \rangle$ for alkali-ions as a function of ion mass from Al₂O₃.](image)
fragmented ions are obtained. The results are shown in fig. 6. The attempt to fit the molecular yields with the sum rule \[ \gamma_{\text{mol}} = \sum \gamma_{\text{atom}} \] fails completely in the mass range above \( m > 100 \text{ amu} \). The sum rule predicts increasing yields with increasing mass. The measured values suggest that the yields are nearly independent of ion mass in the high mass regime. The high electron yield for the Gramecidine ion \((m=1882)\) is only describable with a threshold velocity for kinetic electron emission below \( 4 \cdot 10^6 \text{ cm/s} \), which seems reasonable since Beuhler and Friedman \[12\] reported lower threshold velocities for heavy water clusters.

\[
\text{mol. ions } \rightarrow \text{Al}_2\text{O}_3
\]

\( E_{\text{ion}} = 21\text{keV} \)

Figure 6: Summarized electron yields of the molecular- and cluster-ions. \((M+1)^+\) means the intact protonated molecular ions of Glycine, Valine, Phenylalanine and Gramecidine.

\[
\langle \gamma \rangle \text{ (electrons/ion)}
\]

\[
E_{\text{ion}} = 21\text{keV}
\]

Figure 7: Electron yields for the alkali-ions obtained from the CsI-electrode.

\text{CsI-electrode}

The electron yields from CsI are about one order of magnitude higher than those of Al\(_2\)O\(_3\) but the dependence on mass is nearly the same in the case of monoatomic ions. The yields and the calculated values are presented in fig. 7. The molecular ions show a clear maximum at about \( m \approx 20 \).
amu in contrast to the Al₂O₃-electrode, and the sum rule fails in the whole mass range. The mass
dependence seems to be well describable by a smoothed function, that means, that the yields are
nearly independent on composition and structure of the molecular ions. Nevertheless, the yields of
molecular ions are nearly twice the yields of the monoatomic ions.

![Graph showing yield vs. mass for CsI](image)

**Figure 8: Yield <γ> of the molecular ions from CsI.**

**Detection efficiency**
The frequency distributions of the secondary electrons are well described by polya distributions and
the detection efficiency, which can be written as

$$ P = 1 - w_0, $$

where \( w_0 \) is the probability that no electron is emitted during the ion impact. \( P \) is therefore given by

$$ P = 1 - (1 + \gamma \cdot b)^\frac{1}{b}. $$

The factor \( b \) is the scaling parameter of the polya distribution and can be interpreted as the value
describing the deviation from a poisson distribution. All obtained \( b \)-values are in the range between
0 and 0.2, with the higher values from Al₂O₃ obviously caused by a nonhomogenous surface. In the
case of Al₂O₃ the efficiency ranges from 85 % for H⁺ to 87 % for K⁺ for the monoatomic ions and
is above 98 % for the molecular ions. With the CsI-electrode detection efficiencies greater than 99 % for
all investigated ions were calculated.

**Ion multiplicity**
A well known effect in heavy ion induced desorption of secondary ions is the occurance of ion mul-
tiplicity, which means, that two or more identical ions are desorbt simultanously. If two ions strike
the converter electrode the mean number of ejected electrons is twice the value for a single ion. The
obtained pulse height distribution of secondary electrons contains contributions of these events and
are well resolved in the case of the CsI-electrode as shown in fig. 6. Based on the assumption of
a poisson distribution for the ion multiplicity it is possible to deduce the yield of Cs⁺ ions from a
CsI-sample by estimating the frequencies of one detected ion and two ions. Taking the transmission
of the spectrometer into account the yield of Cs⁺ was found to be 1.8 ± 0.2 ions per fission fragment.
This value is in good agreement with previous results of Becker and Wien [13], [14]. It should be
mentioned that the often bad known starting rate of ion desorption was not needed to calculate the
ion yield.
Figure 9: Pulse height distribution of secondary electrons ejected by Cs$^+$ impact on CsI. Quite obvious are the contributions of two an three ions reaching the ion to electron converter simultaneous. The background at low electron numbers is probably caused by neutralized Cs$^+$ ions, which were not postaccelerated.

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