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Distributions of ion-molecule reactions on the crossing of the focused photon beam with an effusion molecular beam

Rozkłady reakcji jonowo-molekularnych na skrzyżowaniu zogniskowanej wiązki fotonów z efuzyjną wiązką molekularną

1. INTRODUCTION

Effusion molecular beams generated directly by effusive channels show very high non- homogeneity in both the longitudinal and transverse directions with respect to the molecular beam axis. Owing to their high intensity, we are interested only in beams generated directly by effusion channels. The system of intersecting effusion molecular and electron or photon beams is successfully used in many investigations of ionisation processes in gases [1–4]. The crossing of molecular and pulsed laser beams was used by Michalak et al. as an ion source of time-of-flight mass spectrometer for investigation of the generation of 118.2 nm light by frequency tripling of 354.6nm radiation [5]. Steenvoorden et al. used this system of beams for investigation of the temperature dependence of the photoionization mass spectra of some hydrocarbons [6].

In the papers [2,7] Michalak and co-workers presented investigations of ion/molecule reactions as an effect of crossing highly non-homogeneous CH_4 and H_20 effusion molecular beams with an electron beam. Displacement of the electron beam along and transverse to, the effusive molecular beam enabled the authors to distinguish zones of different intensity of effusion CH_4 and H_20 beams, where respective ion/molecule reactions took place. In the recent paper [8] the authors presented computer calculations of the influence of the geometrical parameters and the mutual configuration of an effusion capillary and a focused photon beam on the number of generated ions on the crossing of the photon and molecular beams.

Figure 1 shows the intersection of the effusion molecular beam with a focused photon beam just above the capillary outlet in the open ion source of a mass spectrometer. For two reasons: i.e. the photon beam is focused (different density distribution of photons along the photon beam), and the intersection occurs where the molecular beam intensity gradient is very high, it is evident that the intensity of the generated photo-ion beam is greatly affected by the position of the photon beam with respect to the capillary outlet.

In this work the authors present computer calculations of distribution of ion/molecule reactions on the crossing of focused photon and effusion molecular beams as a function of the geometrical parameters of the effusion capillary (h and R are the length and radius of the capillary, respectively) and the position of the photon beam with respect to the capillary outlet (d is the distance between the capillary outlet and the photon beam axis; s_1 and s_2 are displacements of the capillary with respect to the focus of the photon beam) (see Fig. 1). The unit of all the parameters described the ionisation system is the radius R of the effusion capillary. The diameter D of the incident photon beam, the focal length f of used lens, the length L of the focused beam and the wavelength λ of light have in our calculations established values i.e. D = 10R, f = 350R, L = 20R and λ = 0.0002R [8].

The number of primary ions produced by photoionization in a gas unit volume, during a unit time is proportional to the number of molecules in a unit volume and to the density of photons in the photon beam. The intensity I_p of the primary photo-ion current is

$$I_p = \sigma_{h\nu}\, n\, I_{h\nu}\, L \tag{1}$$

where $\sigma_{h\nu}$ is the photo-ionisation cross-section, n — is the number of molecules in the unit volume, $I_{h\nu}$ is the intensity of photon beam, L is the length of a photon beam.

The intensity of the secondary ions is generally smaller by two or more orders of magnitude than that of primary ions, i.e. only a small percentage of primary ions undergoes collision with gas molecules. The intensity of a secondary ion is proportional to the cross-section σ_s of the ion-molecule reaction, the primary current I_p, and the concentration n of the gas molecules:

$$I_s \sim \sigma_s I_p\, n \tag{2}$$

Therefore

$$I_s \sim n^2 \tag{3}$$

It should be remarked that only bimolecular reactions are observed at a pressure of about 10^{-4} Torr, since the probability of a subsequent reaction of a secondary ion with a gas molecule is extremly low. Furthermore, since $I_s \ll I_p$, only those ion-molecule reactions can be traced which occur at nearly every collision, i.e. which have practically no activation energy. In other words, only exothermic or thermoneutral reactions will generally be detected in a conventional mass spectrometer. Production of secondary ions by ion/molecule reactions take place in and partially above the photon beam, where respective ion molecule reactions can take place owing to the high intensity of the molecular beam [2,7].

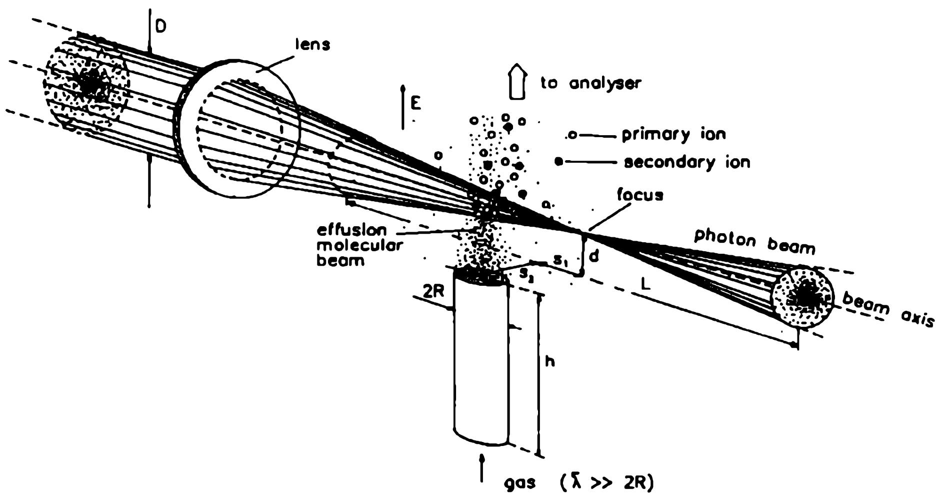


Fig. 1. Intersection of the effusion molecular beam with a focused photon beam in the open ion source of a mass spectrometer
Skrzyżowanie efuzyjnej wiązki molekularnej z zogniskowaną wiązką fotonów w otwartym źródle jonów spektrometru mas

2. CALCULATION PROCEDURE AND RESULTS

In this work we have applied a calculation procedure described previously for the crossing of electron or photon beams and molecular beams in an open ion source of a cycloidal mass spectrometer [8–11]. In this procedure we divide a photon beam into many elementary elements and then we calculate the number of molecules effusing from a cylindrical capillary in each of these elements. Therefore we can calculate a concentration, n, of effusing molecules in any area of a photon beam or an average concentration of molecules in a whole photon beam.

Figure 2 shows the influence of the distance d of the photon beam from the capillary outlet on the number of generated primary and secondary ions in this beam for the length $h = 0$ (Knudsen's cell) of the effusion capillary. The photon beam is in the central position ($s_1 = s_2 = 0$) with respect to the capillary outlet. Decreasing dependance of the number of primary and secondary generated ions with the distance d results from decreasing intensity of effusion molecular beams for bigger distances d. The lower values of the number of generated secondary ions in comparision to primary ions is also evident.

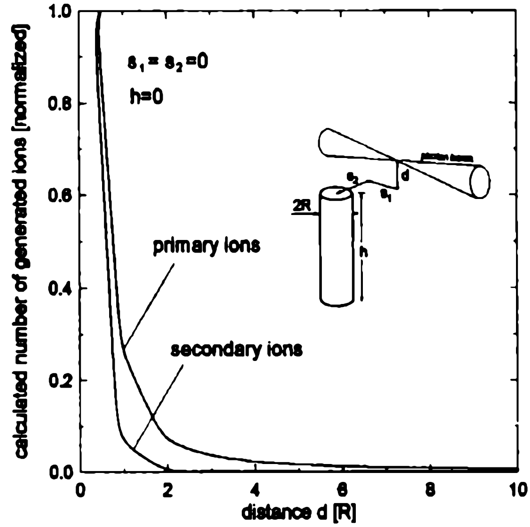


Fig. 2. The number of generated ions in the focused photon beam crossed by a molecular beam as a function of the distance d for the length of the effusion capillary $h = 0$. The photon beam is in the central position with respect to the capillary outlet i.e. $s_1 = s_2 = 0$
Liczba generowanych jonów w zogniskowanej wiązce fotonów przecinanej wiązką molekularną jako funkcja odległości d, w przypadku, gdy długość kapilary efuzyjnej $h = 0$. Wiązka fotonów znajduje się w centralnej pozycji względem wylotu kapilary, tj. $s_1 = s_2 = 0$

In the used calculation procedure of the number of generated ions in the focused photon beam crossed by the effusion molecular beam we can also observe the distribution of generated ions along the axis of the photon beam [8]. Figure 3 shows distributions of the number of generated ions along the photon beam crossed by an effusion molecular beam formed by the effusion hole ($h = 0$) for the distance $d = 0.5R$ and the central position ($s_1 = s_2 = 0$) of the focus of the photon beam with respect to the capillary outlet. In accordance with expectation most of primary and secondary ions are generated in the area of the focus of the photon beam. For the presented position ($s_1 = s_2 = 0$) of the focus of the photon beam and a short distance d, about 90% of ions are produced in a very small area (L = 1R) around the focus.

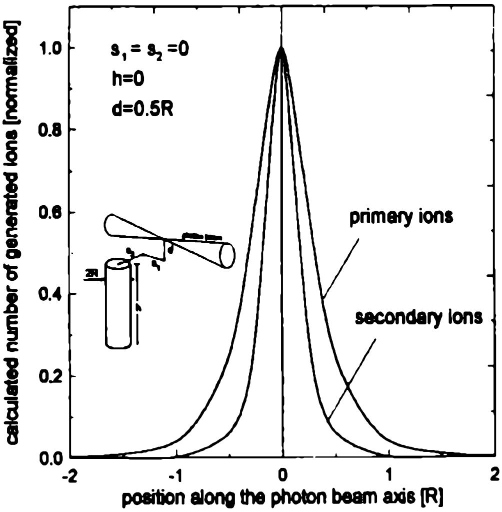


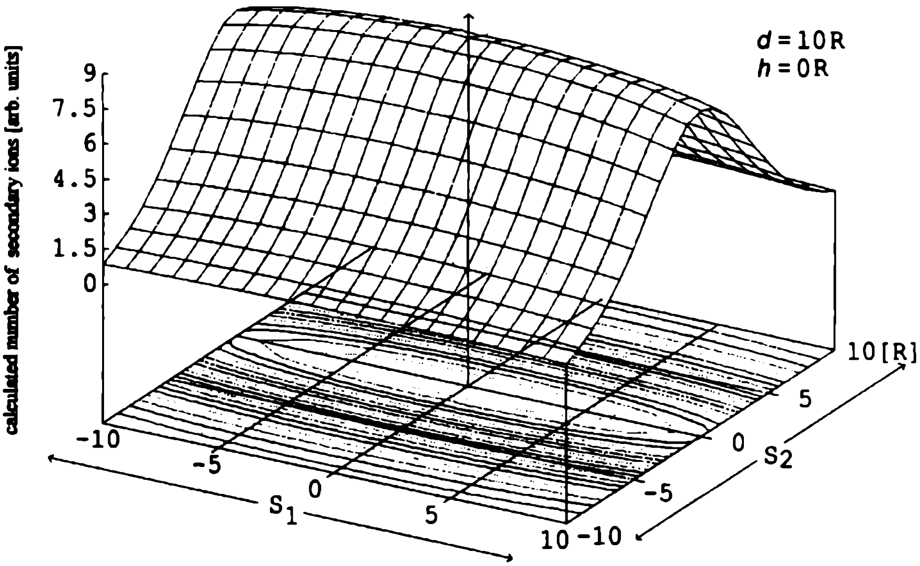
Fig. 3. The number of generated ions along the photon beam for the central positon ($s_1 = s_2 = 0$) of the focus of this beam with respect to the capillary outlet. The effusion molecular beam is formed by the effusion hole ($h = 0$) and the distance d = 0.5R

Liczba generowanych jonów wzdłuż wiązki fotonów przy centralnej pozycji ogniska ($s_1 = s_2 = 0$) względem wylotu kapilary. Efuzyjną wiązkę molekularną formuje otwór efuzyjny ($h = 0$) w odległości d = 0,5R

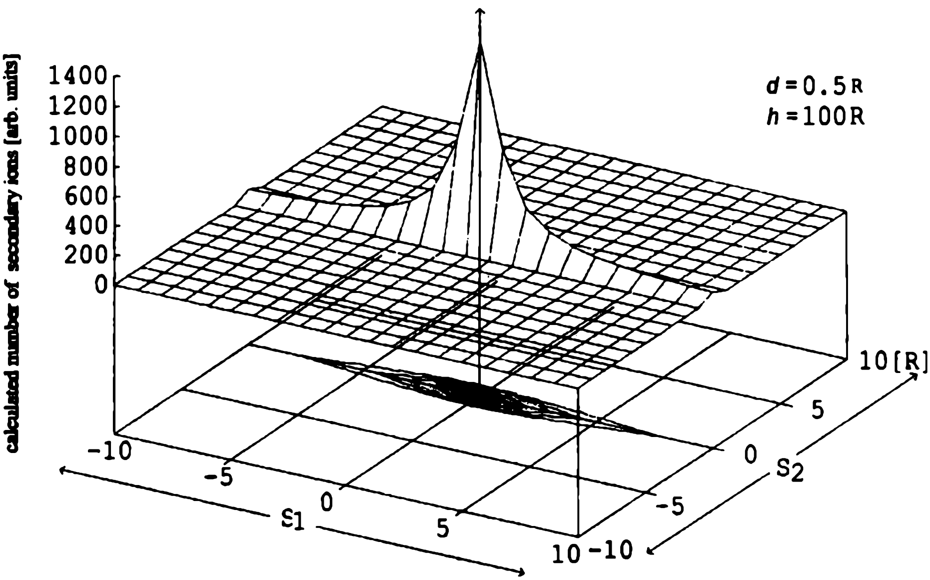
The summarized effects of production of secondary ions in the focused photon beam crossed by a molecular beam are presented in Figures 4*a–d*. In these cases a molecular beam is formed by the capillaries of length h = 0 and 100R and the number of generated ions was calculated for different positions of the focus of the photon beam in the plane $s_1 s_2$ and for the established distance d.

The ordinates in the presented results show the number of generated ions in the focused photon beam in relative units, but the scale used here being common for all the figures in Figs. 4*a–d*. in order to get results which will be comparable. The differences between results obtained for the capillary of length h = 0 and h = 100R result from the collimation effect of molecular beam by longer capillaries. For the established length h of capillary (h = 100R, see Figs. 4*b*, *c*, *d*) the number of generated secondary ions for higher distances d is adequately lower. For bigger distances d from the capillary outlet a gradient of concentration, n, of molecules in a molecular beam is adequately lower, too.

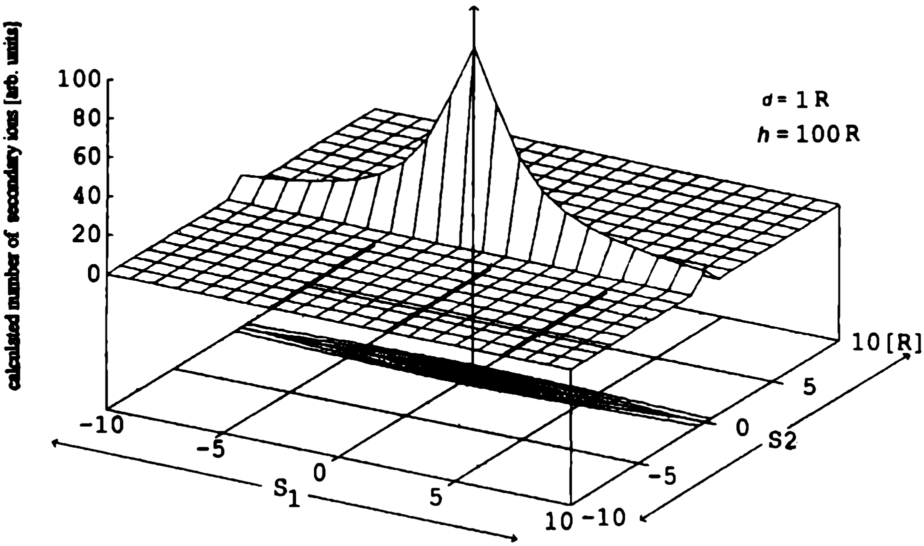
a)


calculated number of secondary ions [arb. units]
9
7.5
6
4.5
3
1.5
0
d = 10R
h = 0R
-10
-5
0
5
10
S1
-10
-5
0
5
10 [R]
S2

b)


calculated number of secondary ions [arb. units]
1400
1200
1000
800
600
400
200
0
d = 0.5R
h = 100R
-10
-5
0
5
10
S1
-10
-5
0
5
10 [R]
S2

c)



d)

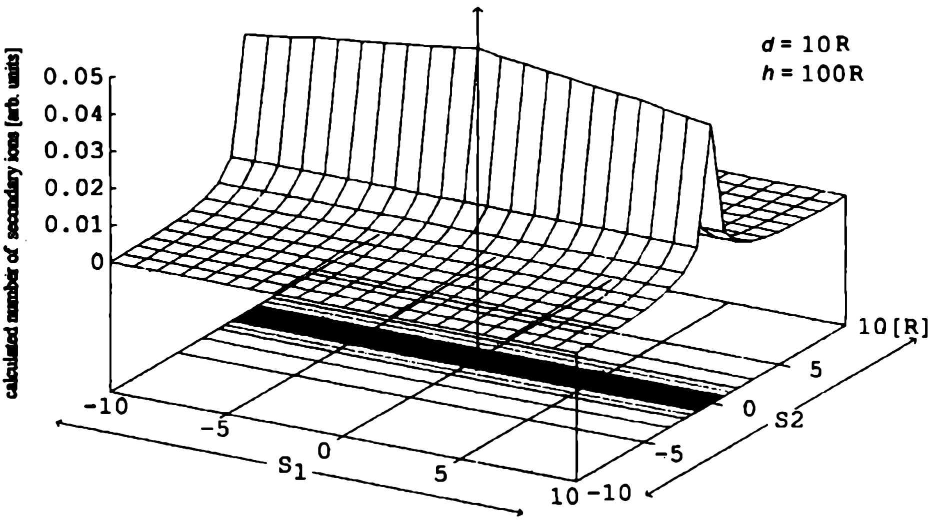


Fig. 4 a b c d. The number of generated secondary ions in the focused photon beam crossed by a molecular beam in the plane s_1s_2. The molecular beam is formed by the capillary $h = 0$ (*a*) and $h = 100R$ (*b*, *c*, *d*). The distance *d* is: $d = 10R$ (*a*); $d = 0.5R$ (*b*); $d = 1R$ (*c*); $d = 10R$ (*d*)
Liczba generowanych jonów wtórnych w zogniskowanej wiązce fotonów przecinanej wiązką molekularną w płaszczyźnie s_1s_2. Efuzyjna wiązka molekularna jest formowana przez kapilarę o długości $h = 0$ (a) oraz $h = 100R$ (*b*, *c*, *d*). Odległości: $d = 10R$ (*a*); $d = 0,5R$ (*b*); $d = 1R$ (*c*); $d = 10R$ (*d*)

3. CONCLUSION

In this work the computer calculations of the number of generated secondary ions by ion/molecule reactions in the focused photon beam crossed by an effusion molecular beam as a function of the geometrical parameters of the effusion capillary, the parameters of photon beam and the position of the photon beam with respect to the capillary outlet is presented. In the used calculation method we can observe not only a total number of generated secondary ions on the crossing of photon and molecular beams but also a production of ions in any area of a photon beam. These observations are very difficult in the real photon beam. The results and method presented here can be applied in the construction of ion source of mass spectrometers utilizing the intersection of a non-homogeneous effusion molecular beam with a focused photon beam for the observation of ion/molecule reactions.

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STRESZCZENIE

W niniejszym artykule przedstawiono rezultaty komputerowych obliczeń rozkładów reakcji jonowo-molekularnych na skrzyżowaniu zogniskowanej wiązki fotonów z efuzyjną wiązką molekularną w otwartym źródle jonów spektrometru mas. Rozkłady te rozpatrzono w zależności od geometrycznych parametrów kapilary efuzyjnej, parametrów wiązki fotonów oraz jej pozycji względem wylotu kapilary.