

NOTIZEN

Electron Emission of CuBe on Bombardement with Parent and Fragment Ions of Ammonia and Phosphine

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(Z. Naturforsch. **32a**, 1559—1560 [1977];
received October 26, 1977)

The secondary electron emission of the first dynode of a CuBe-alloy sixteen dynode electron multiplier has been studied in the course of electron impact ionization studies of ammonia and phosphine. Relative secondary electron emission coefficients have been obtained for the singly and doubly charged parent and fragment ions of ammonia, ammonia-d₃, phosphine and phosphine-d₃ for kinetic energies of 5.25 and 10.5 keV. It has been found that in general deuterated ions have smaller γ coefficients than protonated ions, that ammonia ions have larger γ coefficients than phosphine ions, and that the γ coefficient increases with the complexity of the ion under study.

1. Introduction

The increased use of electron multipliers as detectors of positive ions in mass spectrometers makes a more detailed knowledge of the electron emission due to ion bombardment desirable. The processes which can occur at the first dynode of the multiplier can be divided into two effects. At low energies (below 500 eV), Auger neutralization of the ions results in a type of emission usually classified as potential electron emission. Above 500 eV, electron ejection occurs dominantly by the transfer of kinetic energy from the impinging ion to the metal. This type of emission is usually classified as kinetic electron emission. The secondary electron emission coefficient γ equals the total number of electrons released per impacting ion. The gain G of an electron multiplier is defined as $G = \gamma \beta^n$, with β the electron-electron emission coefficient of the n dynodes.

Secondary electron emission is affected by the energy and type of the impinging ions, as well as the material and preconditioning of the surface of the first dynode. In this paper the parent and fragment ions of the polyatomic molecules NH₃ and PH₃, as well as their deuterated species have

been studied in order to obtain information about the mass dependence and the dependence on the complexity of the ion.

2. Experimental Procedure

The electron multiplier gain has been measured using ions produced, analyzed and monitored in a Varian MAT, type CH5 mass spectrometer. It is a double focussing sector field mass spectrometer of resolving power 30000 (10% vally) with a differentially pumped analyzer head containing an electron impact ion source with an open housing for molecular gases. Ions formed in this source are extracted and focussed by various drawing out electrodes. The mass analyzed ion beam passes the exit slit of the mass analyzer and a shielding grid electrode before striking the first dynode of the electron multiplier (angle of incidence about 45°). The Allen type electron multiplier has a total of sixteen CuBe alloy dynodes. A moveable Faraday cup collector can be inserted between the exit slit and the shielding grid electrode in order to measure the ion beam current directly.

Gain values for the different ions under study are obtained by alternate measurements with the electron multiplier and the Faraday cup collector. The operating voltage of the electron multiplier has been chosen relatively low, i.e. 2.25 kV, giving an overall accelerating potential for the ions of 5.25 kV. The background pressure in the electron multiplier housing was between about 10⁻² and 10⁻³ Pa during the measurements. Hence, gain values obtained in the present study relate to impact on a gas covered surface under standard mass spectrometric operating conditions.

To be able to compare the present data and in order to eliminate the influence of fatigue and surface changes the gain of each ion under study is normalized with a simultaneously measured reference ion, i.e. mixing each sample gas with argon and relating the determined gain value of the ion under study $G(\text{ion}) = \gamma(\text{ion}) \beta^n$ to the gain value observed for argon $G(\text{Ar}^+) = \gamma(\text{Ar}^+) \beta^n$, yielding a relative secondary electron emission coefficient $\gamma' = G(\text{ion})/G(\text{Ar}^+) = \gamma(\text{ion})/\gamma(\text{Ar}^+)$. The estimated relative precision of the measurement of γ' corresponds to an average deviation of about $\pm 5\%$.

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Table 1. Relative secondary electron emission coefficient. $\gamma' = \gamma$ (ion under study)/ $\gamma(\text{Ar}^+)$ for various parent and fragment ions of NH_3 , ND_3 , PH_3 and PD_3 impacting on a CuBe alloy dynode. Singly charged ions have a kinetic energy of 5.25 keV and doubly charged ions of 10.5 keV.

ion	mass	γ'	deut.ion	mass	γ'
NH_3^+	17	1.32	ND_3^+	20	1.25
NH_2^+	16	1.23			
NH^+	15	1.13			
N^+	14	1.0			
H_2^+	2	0.91			
H^+	1	0.78			
NH_3^{++}	17	1.79	ND_3^{++}	20	1.57
PH_3^+	34	1.14	PD_3^+	37	1.09
PH_2^+	33	1.09	PD_2^+	35	1.06
PH^+	32	1.04	PD^+	33	1.02
P^+	31	0.97			
H_2^+	2	0.80	D_2^+	4	0.79
H^+	1	0.78	D^+	2	0.57
PH_3^{++}	34	1.52	PD_3^{++}	37	1.50
PH_2^{++}	33	1.42	PD_2^{++}	35	1.32
PH^{++}	32	1.38	PD^{++}	33	1.32
P^{++}	31	1.32			

3. Results

The relative secondary electron emission coefficient has been measured for parent and fragment ions^{1, 2} of ammonia and phosphine, where ions have been produced with an ionizing electron energy of

70 eV. The results obtained are presented in Table 1. It can be seen that (1) in general deuterated ions have smaller γ' coefficients, that (2) parent and fragment ions of ammonia have larger γ' coefficients than the corresponding ions of phosphine, and that (3) the γ' coefficients increase with the complexity of the ion studied.

All three findings are consistent with the approximate result obtained by Van Gorkom and Glick³, that the emission coefficients for atomic particles with the same velocity and different mass are proportional to the square root of the ion mass, taking into account the Inghram and Hayden⁴ model of breakup of the molecular ion upon collision followed by independent action by the resulting particles on the surface of the solid.

Acknowledgement

The author is indebted to the Österreichischer Fonds zur Förderung der Wissenschaftlichen Forschung for financial assistance under Project Nr. 1490, 1727 and 2781, and to Professor M. Pahl, head of the department, for the opportunity to use the mass spectrometer system VARIAN MAT, type CH 5.

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² T. D. Märk and F. Egger, J. Chem. Phys.; **67**, 2629 [1977].

³ M. Van Gorkom and R. E. Glick, Int. J. Mass Spectrom. Ion Phys. **4**, 203 [1970].

⁴ M. G. Inghram and R. J. Hayden, Mass Spectrometry, Nucl. Sci. Ser., Rep. 14 NAS-NRC, Washington 1954.