

## Partial Cross Sections for Dissoziative Ionization of Fluorinated Compounds by Electron Impact

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### Abstract

Ionization cross sections of fragment ions of  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$ ,  $\text{C}_3\text{F}_8$ ,  $n\text{-C}_4\text{F}_{10}$ ,  $\text{C}_2\text{F}_4$ ,  $1\text{-C}_4\text{F}_8$ ,  $\text{SiF}_4$ ,  $\text{COF}_2$ ,  $\text{CHF}_3$  were determined in dependence on electron energy up to 125 eV by means of a quadrupole mass spectrometer. Tails at the low energy part of the characteristics are interpreted as a result of kinetic energy depending on molecular weight of fragments. Parent ions are only detected for chemically unsaturated compounds showing characteristic curves of ionization efficiency. Total cross sections obey the additive rule.

### 1. Introduction

Plasma of fluorocarbon gases has received considerable attention in silicon semiconductor processing. Ionized and neutral fragments produced by such discharges effect plasma etching and thin film deposition. Electron impact is the most important process in generating these particles. Cross sections of ionization and of dissoziation enable to calculate the plasma kinetics and the plasma-chemical reactions in the molecular gas and at the surface of substrates.

The absolute ionization cross section  $Q$  depending on the nature of gas and the impact energy of electrons  $W$  is given by

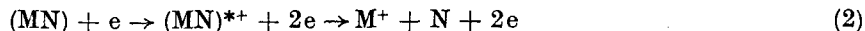
$$Q(W) = \frac{I^+}{I_e} \cdot \frac{1}{n \cdot l} \quad (1)$$

$I^+$ ,  $I_e$  ion, electron current

$n$  particle density

$l$  effective path of electron interaction with the gas

In most cases electron impact ionization in molecular gases is connected with electronical and vibrational excitation, frequently followed by dissoziation



A characteristic spectrum of fragment ions and neutrals is produced by each type of molecules depending on the interaction energy.

An exact calculation of cross sections for this process is a difficult problem of quantum mechanics. Approximation formulae are frequently used to calculate the total ionization cross section [1].

## 2. Experimental

Experiments were carried out by means of a commercial quadrupol mass spectrometer with cross beam ion source which enables to vary the impact energy of electrons in an extended range from 5 to 130 eV. A differentially pumped vacuum system (oil diffusion pump, liquid N<sub>2</sub>-trap, heating at 250°C for several hours) in connection with a special molecular gas flow system provides for an accurate pressure level in the collision region of about 10<sup>-4</sup> Pa independently of the kind of gas and a residual gas pressure smaller than 10<sup>-6</sup> Pa. Single impact can be assumed.

The energy scale and the sensitivity to ion current of the used mass spectrometer were calibrated using Ar with its wellknown properties (Appearance potential 15.76 eV, cross section maximum at 90 eV 2.75 · 10<sup>-16</sup> cm<sup>2</sup> [2]).

$$Q(W) = Q_{Ar}(W) \cdot \frac{I^+}{I_{Ar}^+} \quad (2)$$

Constant sensitivity over the full mass range is obtained by a method described in [3].

## 3. Results and Discussion

All measured ionization efficiency curves are characterized by long tails. The onset energy is very much lower than the appearance potential calculated from the linear part of the ion current energy plot. A reason for that may be vibrational excitation of the molecules which support the dissoziation process with energies of some tenths eV. However, a large part of energy results from the voltage drop over the electron emitting cathode and from the penetration of the ion removal field into the collision chamber. These effects cause a width of energy distribution of electrons of some eV.

The molecule receives ionization energy as well as an additional amount of energy by electron impact. This energy causes dissoziation. The remaining excess energy occurs as kinetic energy of fragments of the molecule. Calculation is a hard problem.

Excess energy must be gathered additionally to the energy of dissoziation and ionization by the electrons. Consequently the appearance potential shifts to a higher value. In agreement with momentum and energy conservation law the kinetic energy is distributed to neutral and ionized fragments according to

$$W_{\text{kin}} = \left(1 - \frac{M^+}{M + N}\right) \cdot W_{\text{exc}} \quad (4)$$

$M, N$  molecular weight of fragments

$W_{\text{kin}}$  kinetic energy of ion

Small fragment ions from ponderous molecules (for instance CF<sup>+</sup>/C<sub>3</sub>F<sub>8</sub>) provide for a large portion of kinetic energy. Parent ions (Ar<sup>+</sup>, C<sub>2</sub>F<sub>4</sub><sup>+</sup>, C<sub>4</sub>F<sub>8</sub><sup>+</sup>) can not have kinetic energy and give the smallest energy values therefore. The energy width  $W_0$  of Fig. 1 summarizing all energy distributing effects was estimated from the ion current  $I'$  at the appearance potential  $W_i$ .  $W_i$  results from linear extrapolation of the high energetic part of the ion current to  $I = 0$  (Fig. 1a).

Assuming a constant energy distribution in the energy intervall of electron collision energy and in the excess energy of ionization the ion current in the low energetic part follows nearly a cubic curve

$$I = \frac{a}{6W_0^2} (W + W_0 - W_i)^3 \quad \text{for} \quad W_i - W_0 < W \leq W_i \quad (5)$$

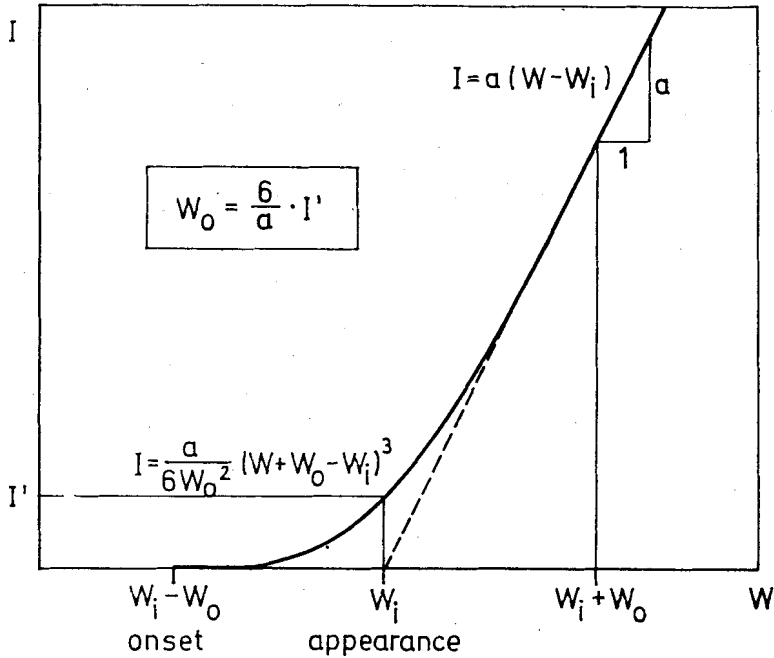


Fig. 1a. Calculation of onset potential and appearance potential  $W_i$  from the ion current — electron energy characteristic

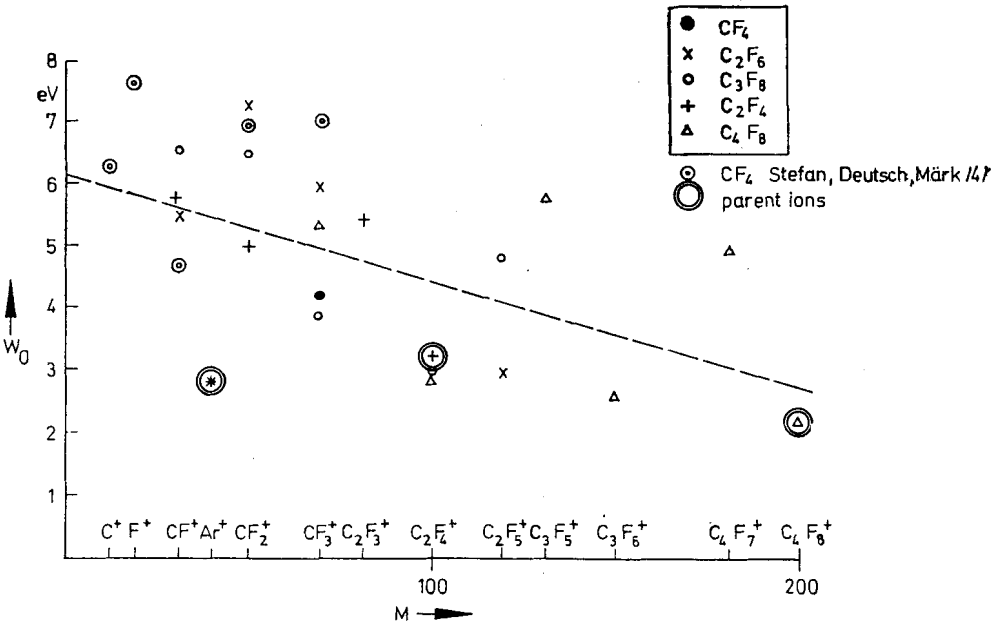


Fig. 1b. The energy  $W_0$  of the tail in Fig. 1a for different fragment ions of the perfluorinated compounds and Ar

which changes over into the following one

$$I = a(W - W_i)$$

at higher energy ( $W > W_i + W_0$ ) in agreement with  $n^{\text{th}}$  root extrapolation. In spite of the large experimental error the fitted  $W_0$  values show a clear increase of excess energy with decreasing mass of fragment ions as a property of fragmentation process. In [1] is reported of  $\text{CF}_3^+/\text{CF}_4$  ions with a kinetic energy of 1...2 eV. Therefore the F-particle must get about 4...7 eV. The very precisely measured cross sections of fragment ions of  $\text{CF}_4$  [4] have long tails indicating a high excess energy level (Fig. 1 b, Fig. 2 a dashed line) too. Especially, the  $W_0$  value 7.6 eV of  $\text{F}^+/\text{CF}_4$  (which well agrees with them of  $\text{CF}_3^+/\text{CF}_4$  of 7.1 eV as consequence of fragmentation) is so high, that  $\text{F}^+$ -ions should be assumed to be not able to escape the collision chamber without interaction with the wall. This may be a reason for the small level of  $\text{F}^+$  ions. We did not observe any peaks of the small ions  $\text{F}^+$  or  $\text{C}^+$  although fragmentation of  $\text{CF}_4$  actually produces large amounts of Fluor.

Deduced from  $W_0$ -values of parent ions  $\text{Ar}^+$ ,  $\text{C}_2\text{F}_4^+$  and  $\text{C}_4\text{F}_8^+$  in Fig. 1 the width of electron energy distribution is about 3 eV.

Tab. 1 presents the calculated appearance potentials  $W_i$  of fragment ions. The values are generally higher than known onset potentials [5] due to the described excess energy. Ionization only needs about 10 eV as it is shown at the parent ions  $\text{C}_2\text{F}_4^+/\text{C}_2\text{F}_4$  and  $\text{C}_4\text{F}_8^+/\text{C}_4\text{F}_8$ . Additionally dissoziation of an F-radical needs about 5 eV ( $\text{CF}_3^+/\text{CF}_4$ ,  $\text{C}_2\text{F}_5^+/\text{C}_2\text{F}_6$ ,  $\text{C}_3\text{F}_7^+/\text{C}_3\text{F}_8$ ) independently of the kind of parent molecule. Production of  $\text{CF}^+$  and  $\text{CF}_2^+$  is carried out through complex crack processes and it needs a higher energy amount.

Fig. 2a—j give corrected dependencies of ionization cross sections on electron energy.

A comparison of fragmentation efficiency enables Tab. II. F-atom splitting from the remaining ion shows a decreasing cross section with increasing molecular weight of parent molecule ( $\text{CF}_3^+/\text{CF}_4$ ,  $\text{C}_2\text{F}_5^+/\text{C}_2\text{F}_6$ ,  $\text{C}_3\text{F}_7^+/\text{C}_3\text{F}_8$ ). This behaviour is noticed also in splitting of  $\text{CF}_3$  radical ( $\text{CF}_3^+/\text{C}_2\text{F}_6$ ,  $\text{C}_2\text{F}_5^+/\text{C}_3\text{F}_8$ ) where, however, the expected  $\text{F}^+/\text{CF}_4$  ion is not observed. A special ion, for instance  $\text{CF}_3^+$  or  $\text{CF}_2^+$ , is produced by different dissoziation steps. Therefore, the cross section of such an ion is very different for several parent molecules (e.g.  $\text{CF}_2^+/\text{C}_3\text{F}_8$ ,  $\text{CF}_2^+/\text{C}_4\text{F}_{10}$ ,  $\text{CF}_2^+/\text{C}_2\text{F}_4$ ).

Tab. I: Appearance potential of fragment ions  $W_i$

	$\text{CF}_4$	$\text{C}_2\text{F}_6$	$\text{C}_3\text{F}_8$	$\text{C}_4\text{F}_{10}$	$\text{C}_2\text{F}_4$	$\text{C}_4\text{F}_8$	$\text{SiF}_4$	$\text{COF}_2$
$\text{CF}^+$	28.7	18.0	21.0	24.2	16.3	24.5		
$\text{CF}_2^+$	22.4	17.3	26.6	20.0	15.5			
$\text{CF}_3^+$	15.9	16.5	15.2	15.0		17.0		
$\text{C}_2\text{F}_5^+$					16.0			
$\text{C}_2\text{F}_4^+$			14.4	17.4	10.3	15.2		
$\text{C}_2\text{F}_6^+$		15.5	15.3	17.0				
$\text{C}_3\text{F}_7^+$						19.0		
$\text{C}_3\text{F}_8^+$						15.5		
$\text{C}_3\text{F}_5^+$				17.5		14.3		
$\text{C}_3\text{F}_6^+$						13.6		
$\text{C}_3\text{F}_7^+$			15.5					
$\text{C}_4\text{F}_7^+$						14.9		
$\text{C}_4\text{F}_8^+$						9.7		
$\text{SiF}_3^+$							14.6	
$\text{COF}^+$								18.5
$\text{COF}_2^+$								14.2

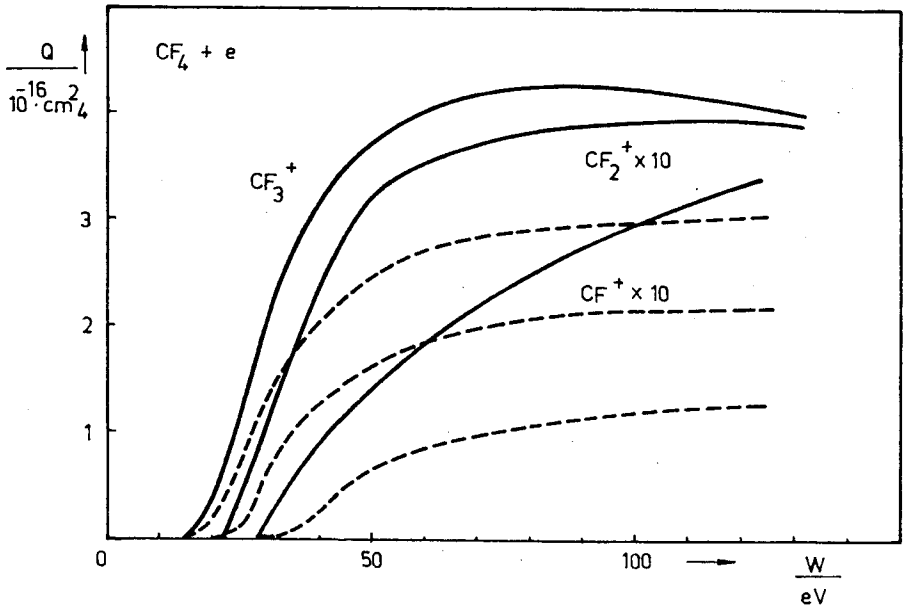


Fig. 2a. Partial cross sections for dissociative ionization vs. electron energy

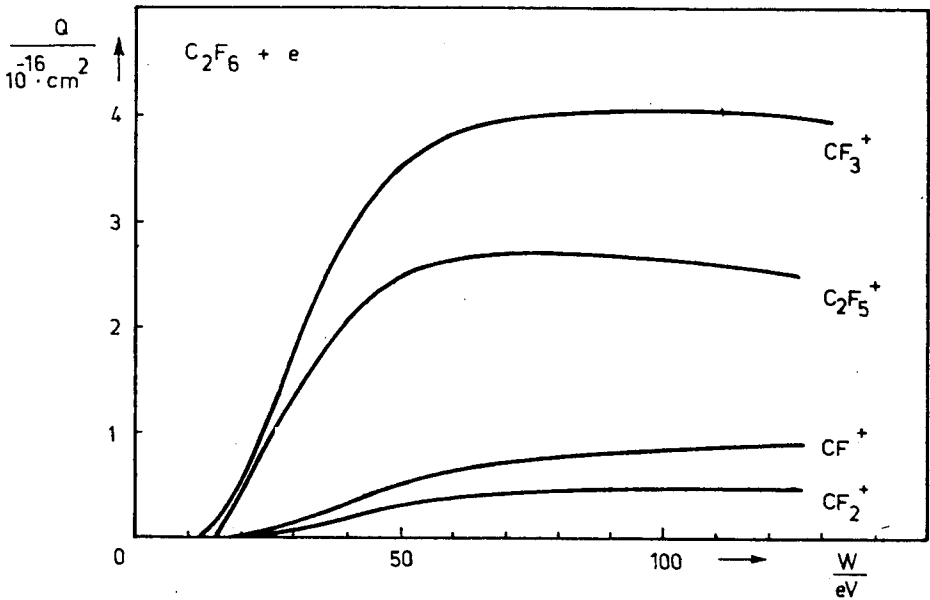


Fig. 2b. Partial cross sections for dissociative ionization vs. electron energy

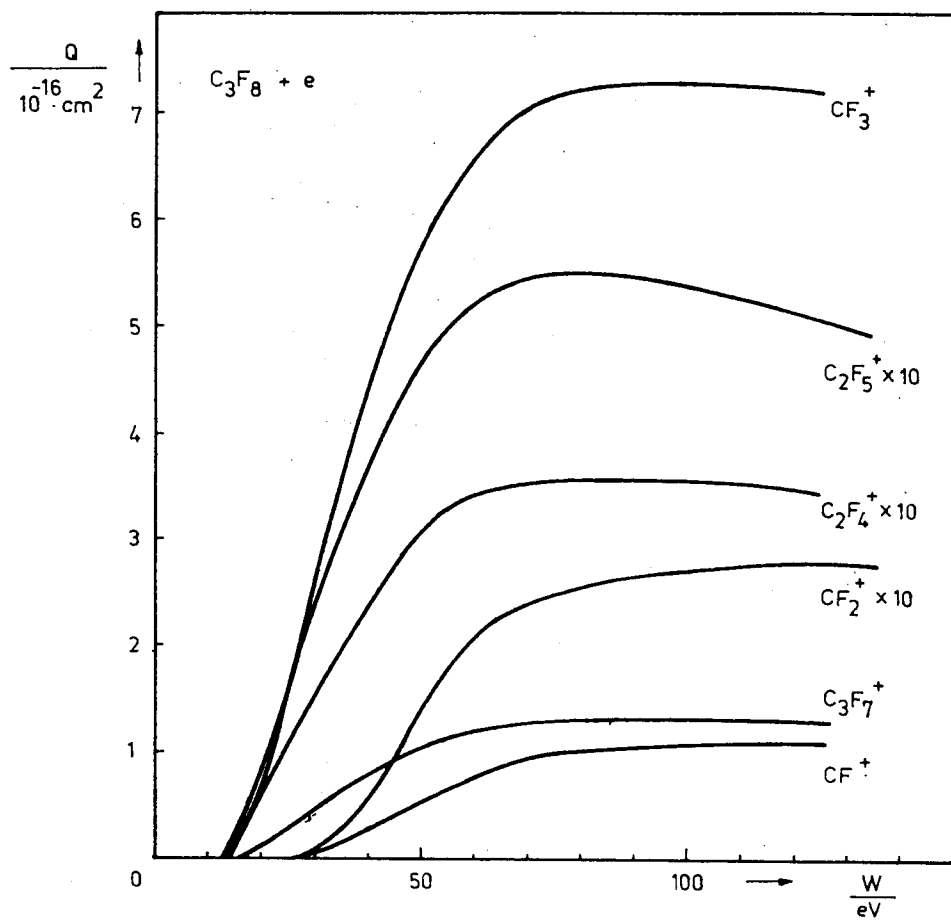


Fig. 2c. Partial cross sections for dissociative ionization vs. electron energy

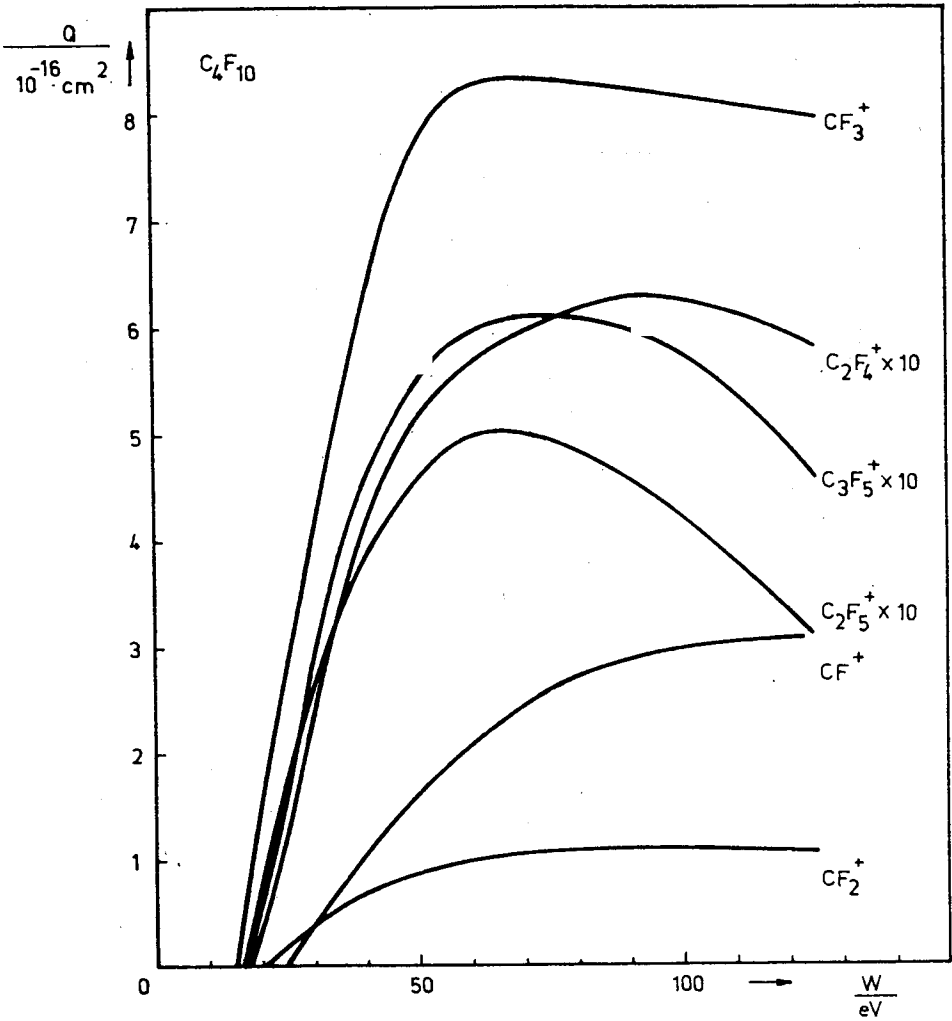


Fig. 2d. Partial cross sections for dissociative ionization vs. electron energy

Parent ions are only observed at the unsaturated perfluorinated compounds  $C_2F_4^+/C_2F_4$  and  $C_4F_8^+/C_4F_8$  (Fig. 2g) showing a particularity:

The cross section characteristics have a shoulder at about 30 eV which indicates that a new ionization mechanism arises, possibly in connection with the double bond of these molecules.

A weak peak of a parent ion was also found at  $SiF_4$  (cross section  $SiF_4^+/SiF_3^+$  at 70 eV about 1%) in agreement with [6].

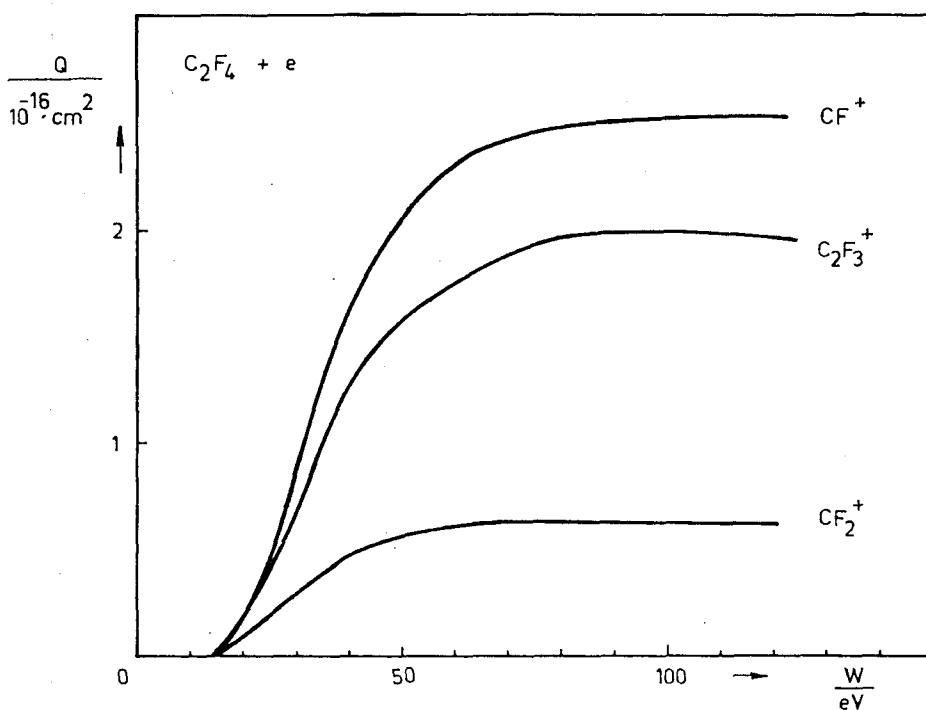


Fig. 2e. Partial cross sections for dissociative ionization vs. electron energy

In literature  $CF_4$  is the best investigated perfluorinated compound [4]. Our measured partial cross sections of its ions  $CF_3^+$ ,  $CF_2^+$  and  $CF^+$  (Fig. 2a) have comparatively large levels but the counted total cross section is within the limits of error of known values (Fig. 3a). The total dissoziation cross section was measured [10] using the pressure increase by electron impact. These cross sections are larger because neutral fragments contribute. However, at energies at 70 eV, the difference is so small, that dissociative ionization seems to be the main process in fragmentation. Calculation according to the additive rule [7] provides total cross sections of all compounds under investigation in a good agreement with the measurements (Fig. 3, Tab. II) especially using the correlation coefficients in [8].



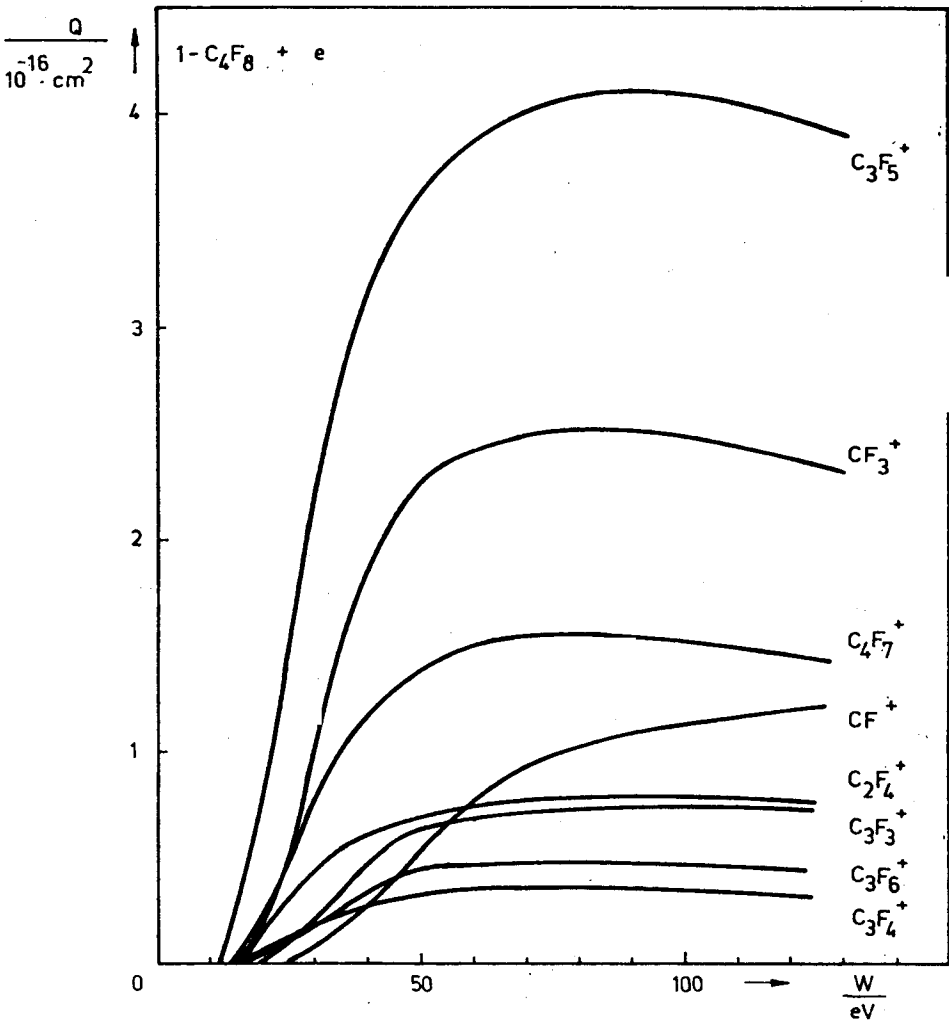


Fig. 2f. Partial cross sections for dissociative ionization vs. electron energy

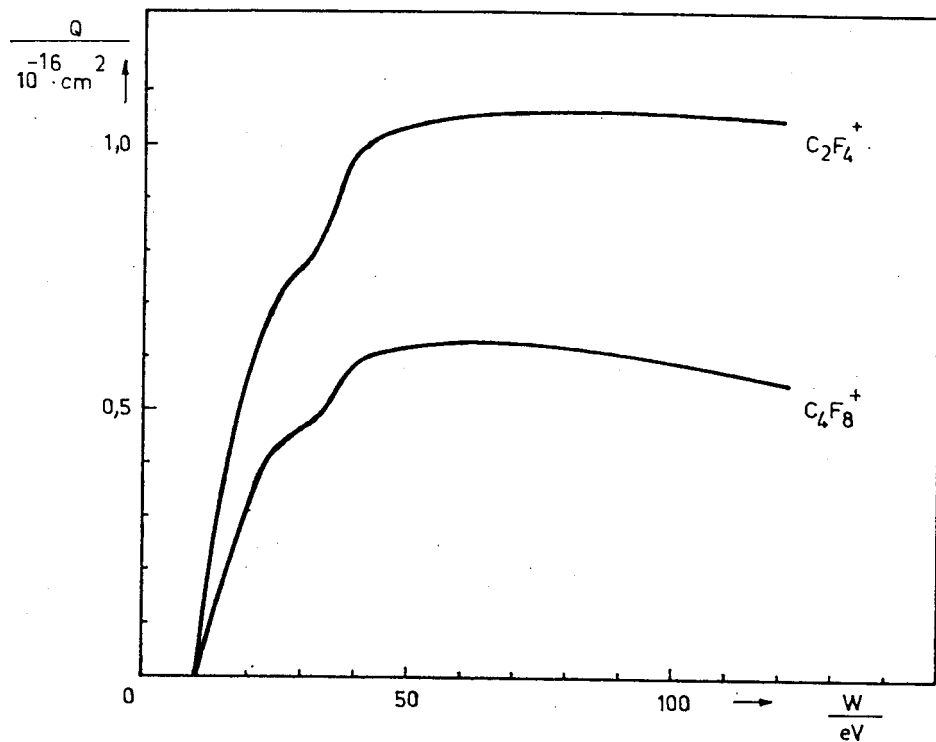


Fig. 2g. Partial cross sections for dissociative ionization vs. electron energy

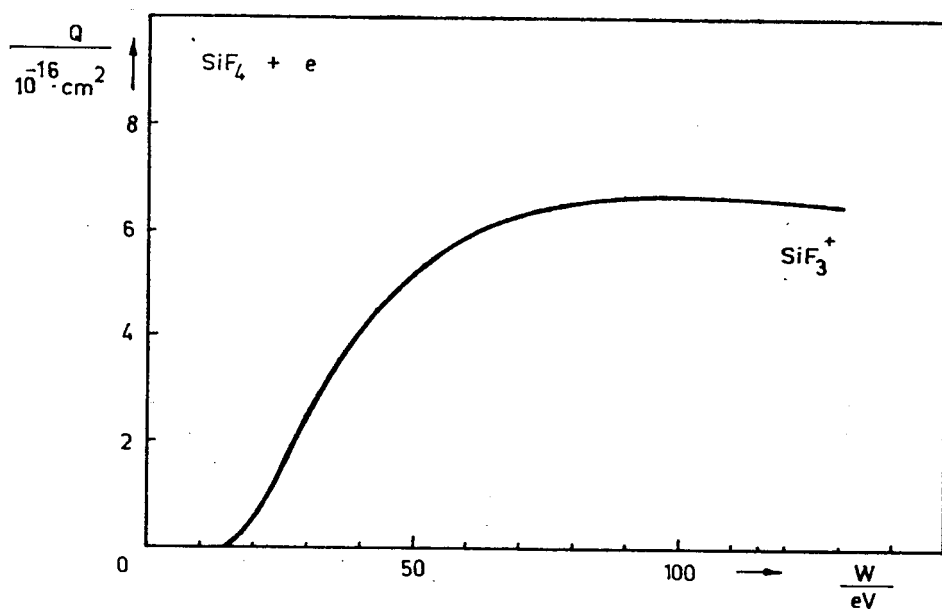


Fig. 2h. Partial cross sections for dissociative ionization vs. electron energy

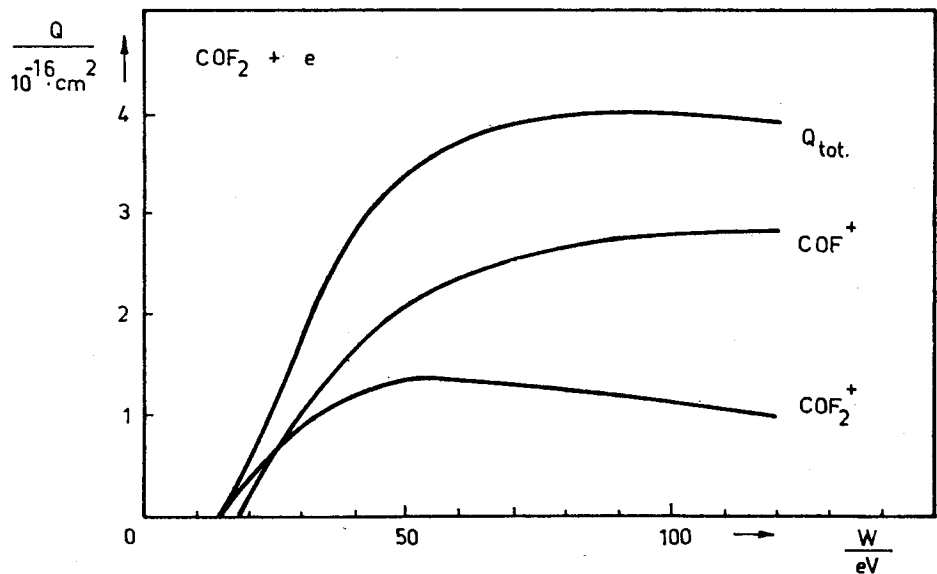


Fig. 2i. Partial cross sections for dissociative ionization vs. electron energy

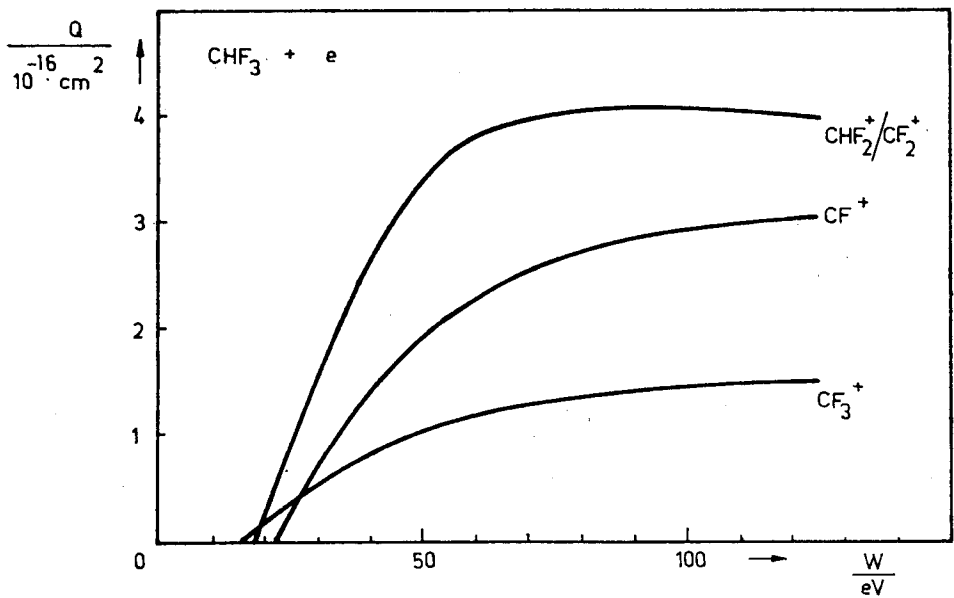


Fig. 2j. Partial cross sections for dissociative ionization vs. electron energy

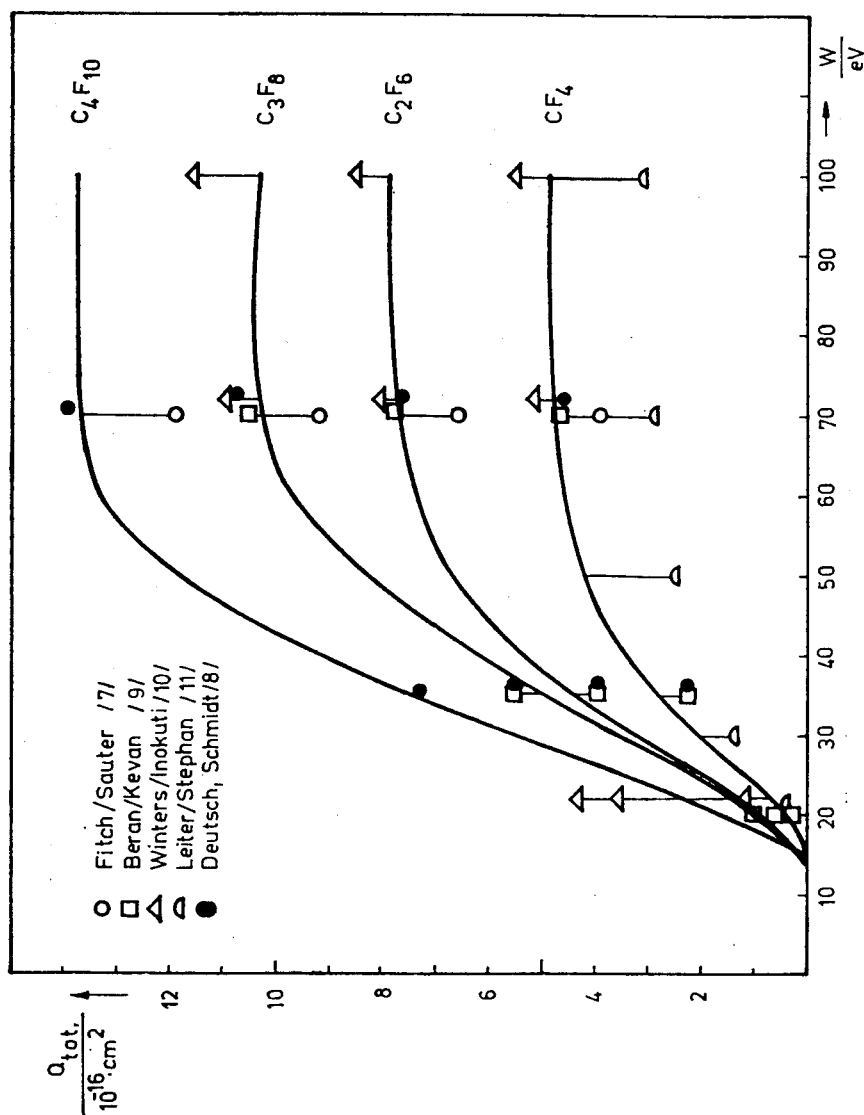


Fig. 3 a, b. Comparison of total ionization cross sections between our experimental results, values calculated using the additive rule [7, 8] and experimental results of other authors for saturated (a) and unsaturated (b) compounds

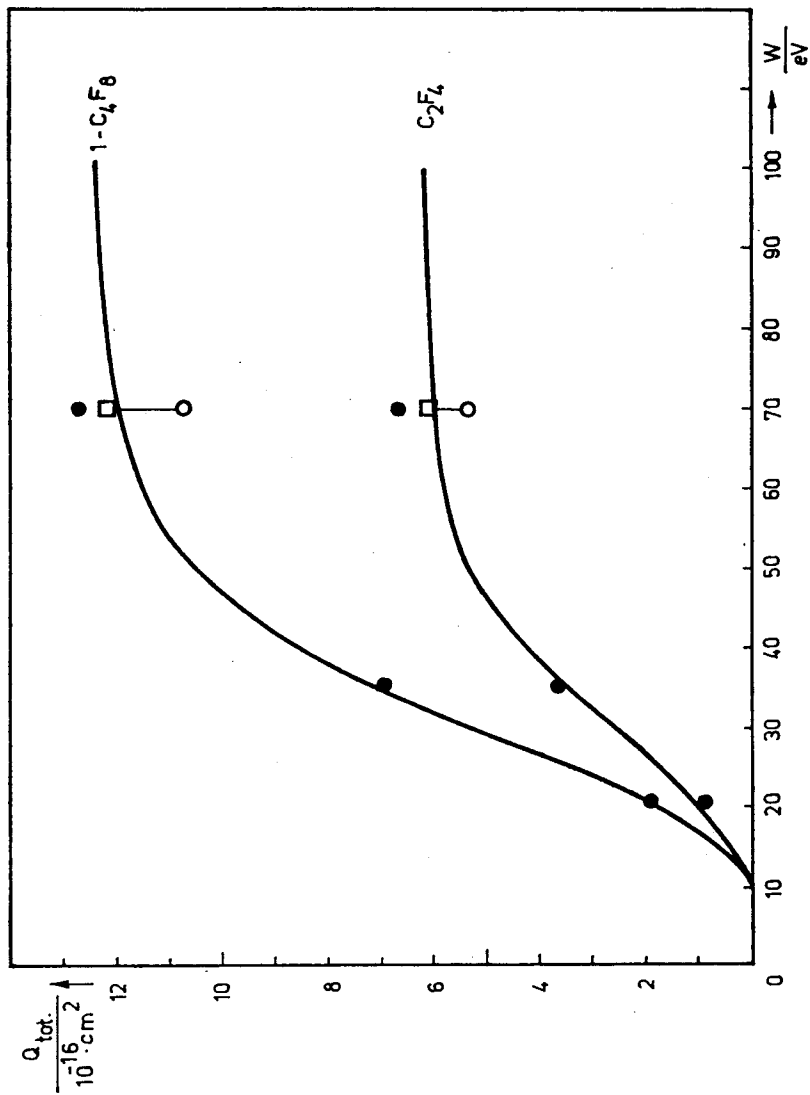


Fig. 3b

Tab. II: Cross section of fragment ions at 70 eV electron energy in  $10^{-18}$  cm<sup>2</sup>

	CF <sub>4</sub>	C <sub>2</sub> F <sub>6</sub>	C <sub>3</sub> F <sub>8</sub>	C <sub>4</sub> F <sub>10</sub>	C <sub>2</sub> F <sub>4</sub>	C <sub>4</sub> F <sub>8</sub>	SiF <sub>4</sub>	COF <sub>2</sub>
CF <sub>4</sub> <sup>+</sup>	0.22	0.75	0.94	2.45	2.36	0.94		
CF <sub>2</sub> <sup>+</sup>	0.37	0.42	0.24	1.05	0.61			
CF <sub>3</sub> <sup>+</sup>	4.22	3.90	7.00	8.33		2.48		
C <sub>2</sub> F <sub>5</sub> <sup>+</sup>					1.83			
C <sub>2</sub> F <sub>4</sub> <sup>+</sup>			0.35	0.60	1.03	0.76		
C <sub>2</sub> F <sub>6</sub> <sup>+</sup>		2.65	0.55	0.50				
C <sub>3</sub> F <sub>7</sub> <sup>+</sup>								
C <sub>3</sub> F <sub>4</sub> <sup>+</sup>						0.72		
C <sub>3</sub> F <sub>5</sub> <sup>+</sup>						0.37		
C <sub>3</sub> F <sub>6</sub> <sup>+</sup>				0.61		4.01		
C <sub>3</sub> F <sub>8</sub> <sup>+</sup>						0.46		
C <sub>3</sub> F <sub>7</sub> <sup>+</sup>			1.28					
C <sub>4</sub> F <sub>9</sub> <sup>+</sup>						1.51		
C <sub>4</sub> F <sub>8</sub> <sup>+</sup>						0.63		
SiF <sub>3</sub> <sup>+</sup>							6.30	
COF <sub>2</sub> <sup>+</sup>								2.40
COF <sub>2</sub> <sup>+</sup>								1.20
$\Sigma Q_i$	4.81	7.72	10.36	13.54	5.83	11.88	6.30	3.60
$Q_{\text{tot}}$ [8]	4.22	7.34	10.46	13.58	6.32	12.56		3.92
$Q_{\text{tot}}$ [9]	4.68	7.79	10.50		6.19	12.25		
$Q_{\text{Diss}}$ [10]	5.20	8.10	11.0					

## Literature

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