TOTAL IONIZATION AND ELECTRON ATTACHMENT CROSS SECTIONS
OF CCl$_2$F$_2$ BY ELECTRON IMPACT [‡]

V.M. PEJČEV, M.V. KUREPA and I.M. ČADEŽ
Institute of Physics, 11001 Beograd, Yugoslavia

The absolute total ionization cross sections from threshold to 250 eV and dissociative attachment cross sections from zero to 10 eV have been measured for the CCl$_2$F$_2$ (dichloro-difluoro-methane) molecule by using a parallel plate condenser type ionization chamber. The maximum of the ionization cross-section curve was found to be at an energy of about 90 eV with a cross section of 1.44×10^{-19} m^2. The attachment cross-section curve shows three peaks, the most intense being at zero electron energy with a cross-section value of 1.80×10^{-20} m^2, and the other two at energies of 0 6 eV and 3 5 eV, respectively. The maximal relative error in cross-section values is 0 08, for electron energies larger than 0 4 eV.

1. Introduction

Attention was drawn to the CCl$_2$F$_2$ molecule in connection with its high electronegativity, making it a good medium in high voltage devices. Ionization and electron attachment processes were studied by Baker and Tate [1], Warren and Craggs [2], Marriott and Craggs [3], Rosenbaum and Neuert [4], Craggs and McDowell [5], Buchel'nikova [6], Hickam and Berg [7] and Christophorou and Stockdale [8].

The CCl$_2$F$_2$ molecule represents also a potential source of chlorine and fluorine atoms in the stratosphere and it is important to know its behaviour when one estimates the impact of human activities on the ozone concentration. This is why it has been studied lately by photon impact by Gilbert et al. [9] and Ajello et al. [10], and electron impact by Chen and Chantry [11], Huebner et al. [12], King and McConkey [13] and Allcock and McConkey [14].

Our preliminary results for ionization were reported by Kurepa and Pejčev [15] and for electron attachment by Pejčev et al. [16].

2. Experimental

The apparatus and procedure used to obtain these cross sections are given in detail by Kurepa et al. [17], so that only a brief description will be given here.

The absolute ionization and dissociative attachment cross sections were determined using the relation

$$\sigma_{\text{i,a}} = (I_\text{i}/I_\text{e})\,(1/nL).$$

where I_i is the total ion current formed by the passage of an electron beam of intensity I_e along a length L inside a gas atmosphere of target molecules with particle density n ($= p/kT$).

Ions were formed inside a parallel plate condenser system with symmetrical potentials with respect to the electron beam final acceleration potential. The electron beam energy half width was 200 meV in these experiments, as obtained from a trochoidal electron monochromator (Stamatović and Schulz [18]), with an intensity of 0.1 μA.

The pressure of the target gas in the range of $10^{-3} - 10^{-2}$ Pa was determined by a constant gas flow method (Fryburg and Simons [19]). The range of the pressure suitable for absolute cross-section measurements was determined by a separate calibration procedure, in which the normalized positive ion current (I_i/I_e) at constant electron energy was measured as a function of the gas pressure in the gas handling system.

3. Results

3.1. Total ionization cross sections

The total ionization cross sections of the CCl_2F_2 molecule were measured in the electron energy interval from the threshold to 250 eV. Numerical values are listed in table 1. To our knowledge, there is no other absolute cross-section measurement published with which present data could be compared.

The electron energy scale was calibrated using the ionization potential of argon.

To our knowledge, there are also no partial ionization cross-section measurements for the CCl_2F_2 molecule, needed for a thorough understanding of the processes leading to ionization of this molecule.

3.2. Dissociative attachment cross sections

The process of dissociative attachment of electrons to the CCl_2F_2 molecule was investigated earlier by Rosenbaum and Neuert [4], Hickam and Berg [7] and Chen and Chantry [11].

Rosenbaum and Neuert [4] identified Cl^- and F^- ions, the first with an appearance potential of 1.1 eV and a maximum at 1.7 eV, the corresponding values for the second being 2.8 eV and 3.8 eV. The Cl^- peak was described as a strong one, and the F^- as moderate in intensity.

The most thorough analysis was done by Chen and Chantry [11] using a mass spectrometer and an ion source with a RPD electron gun. They measured the relative intensity curves of ions Cl^-, Cl_2^-, F^-, $CClF^-$ and CCl_2^- in the electron energy range from zero to 5 eV. Channels of dissociation for the detected negative ion species can be presented as

$$CCl_2F_2 + e \rightarrow CCl_2F_2^- \begin{cases} Cl^- + CClF_2 \\ Cl_2^- + CF_2 \\ F^- + CCl_2F \\ CCl_2^- + F_2 \\ CClF^- + ClF \end{cases}$$

At present there is no information available as to whether the neutral fragments given in this scheme dissociate further, as to the magnitude of the kinetic energy of the dissociation fragments or as to the nature of the angular distribution of the negative ions.

The total dissociative attachment cross-section curve, as obtained in our experiment, is shown in fig. 1. It has an intense peak at zero electron energy, followed by two more maxima, the first at 0.6 eV and the second at 3.5 eV. Earlier results of Buchel'nikova [6] and Christophorou and Stockdale [8] for the total attachment cross sections are given for comparison in fig. 1, too. Values of Buchel'nikova are by a factor of three lower than ours, while data of Christorphorou and Stockdale are lower than ours by 40%. Numerical values of cross sections in the electron energy range between zero and 6 eV are listed in table 2. In the electron energy range from zero to 0.4 eV our cross-section values are systematically lower than the real ones due to difficulties in handling the low-energy electron beam.

Table 1
Total ionization cross section of the CCl_2F_2 molecule by electron impact in units of $10^{-19} \ m^2$

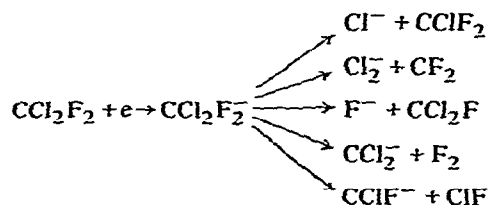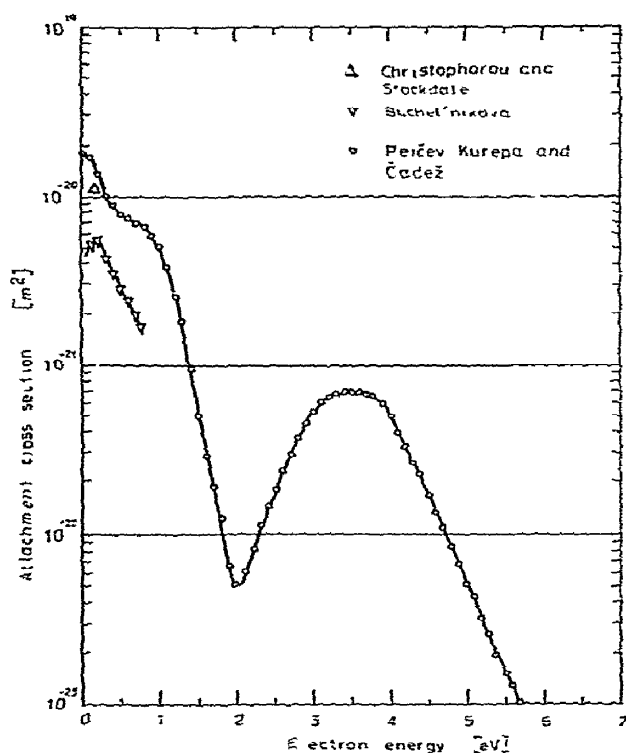| Electron energy (eV)	Cross section	Electron energy (eV)	Cross section
13	0.024	60	1.38
14	0.069	65	1.40
15	0.127	70	1.42
16	0.191	75	1.43
17	0.263	80	1.44
18	0.341	85	1.44
19	0.414	90	1.44
20	0.484	95	1.44
22	0.615	100	1.43
24	0.731	110	1.43
26	0.834	120	1.43
28	0.927	130	1.42
30	0.998	140	1.40
32	1.06	150	1.38
34	1.11	160	1.36
36	1.15	170	1.33
38	1.18	180	1.31
40	1.21	190	1.28
42	1.23	200	1.26
44	1.25	210	1.23
46	1.27	220	1.21
48	1.28	230	1.18
50	1.30	240	1.16
55	1.34	250	1.14

Fig. 1. Total electron attachment cross section of electrons to the CCl_2F_2 molecule.

Mass-spectrometric analysis of Chen and Chantry [11] showed that at very low electron energies the Cl^- negative ions are formed by dissociation of the $CCl_2F_2^-$ parent negative ions, and that the partial attachment cross-section curve for this process is temperature dependent. At lower temperatures the second maximum at 0.6 eV is clearly visible with a dip around 0 3 eV, while for higher temperatures this dip becomes more shallow giving finally only a shoulder at the place of the second maximum, as is the case in our measurements. The other effect giving the same tendency of smearing out the dip between the first two peaks is the electron beam energy width, which was slightly lower in the experiment of Chen and Chantry [11] than in ours.

Table 2
Total dissociative attachment cross sections of electrons to the CCl_2F_2 molecule in units of 10^{-21} m^2

Electron energy (eV)	Cross section	Electron energy (eV)	Cross section
0.0	18.07	3.0	0.530
0.1	17.13	3.1	0.610
0.2	13.67	3.2	0.655
0.3	9.96	3.3	0 674
0.4	8.89	3.4	0.698
0.5	7.61	3.5	0.700
0.6	7.24	3 6	0.692
0.7	6.77	3.7	0 680
0 8	6.59	3.8	0.635
0.9	5.93	3 9	0.585
1.0	5.10	4.0	0.496
1.1	3.80	4.1	0.395
1 2	2.47	4.2	0.321
1.3	1.79	4.3	0 260
1.4	0.940	4.4	0.217
1.5	0.492	4.5	0.165
1.6	0.283	4.6	0.134
1.7	0.180	4.7	0.109
1 8	0.123	4.8	0.084
1.9	0.065	4.9	0.068
2.0	0 050	5.0	0.052
2.1	0.062	5.1	0.044
2.2	0.082	5.2	0.032
2.3	0.114	5.3	0.026
2.4	0.142	5.4	0.019
2.5	0.180	5 5	0.016
2.6	0.230	5 6	0.013
2.7	0.295	5.7	0.010
2.8	0.378	5.8	0.009
2 9	0.456	5.9	0.008
		6.0	0.007

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