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Electron-chlorine molecule total ionisation and electron attachment cross sections†

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Received 5 September 1977, in final form 17 May 1978

Abstract. Cross sections for absolute total ionisation between 10 and 100 eV, dissociative attachment between 0 and 11 eV, and negative-ion formation between 11 and 100 eV, of the chlorine molecule by electron collision have been measured by using a parallel-plate-type interaction chamber. The maximum of the ionisation curve was found to be at 80 eV with a value of $5.58 \times 10^{-20} \text{ m}^2$. Four dissociative attachment processes peaking at 0.0, 2.50, 5.75 and 9.7 eV, with cross sections of 201.6, 2.84, 4.84 and $0.39 \times 10^{-22} \text{ m}^2$, respectively, were detected. Negative-ion formation cross sections with maxima at 20 and 79 eV, and values of 2.58 and $4.28 \times 10^{-22} \text{ m}^2$, respectively, were found. The relative error, except for the first attachment maximum, is ± 0.20 .

1. Introduction

Recently much attention has been paid to the investigation of laser action from rare-gas-halogen-gas mixtures excited by pulsed high-energy electron beams (Ewing and Brau 1975a, Lorents 1977). Among other halogens, chlorine was also used in these mixtures (Ewing and Brau 1975b, Murray and Powell 1976). The laser action is assumed to come from transitions between states of the rare-gas-halide molecules. Excited states of these molecules can be formed either by collisions of excited rare-gas atoms with halogen molecules, or by a three-body recombination between the rare-gas positive ion and a halogen atomic negative ion. The latter is formed mainly by electron-attachment processes.

To the authors knowledge, no cross section data exist for the electron-attachment cross sections to halogen molecules. For chlorine, the object of our investigation, qualitative results only were obtained by Thorburn (1959) and Frost and McDowell (1960). In both of these experiments electron-attachment processes were detected in the electron energy region between 1.6 and 5 eV.

In this experiment the electron energy region between 0 and 100 eV has been searched for both negative- and positive-ion formation and cross sections have been measured.

† This work was supported by the Republic Council for Scientific Research of S R Serbia, Yugoslavia.

2. Experimental

Full details of the apparatus used in this experiment are given elsewhere (Kurepa *et al* 1974), so that only a brief description will be presented here.

For the absolute cross section determination the equation

$$\sigma = \frac{I_i}{I_e} \frac{1}{nL}$$

was used, where I_i is the total positive- or negative-ion current formed by the passage of an electron beam of intensity I_e along a collector electrode of length L , inside the target-gas atmosphere of particle density n ($= p/kT$).

The interaction chamber used in our experiment was a parallel-plate condensor system, introduced by Smith (1930) and Tate and Smith (1932), used thereafter by many authors. The electron beam from an electron gun was energy selected by a trochoidal electron monochromator (Stamatović and Schulz 1968). In the present measurements the electron beam had a half-width of 200 meV and an intensity of 0.1 μ A.

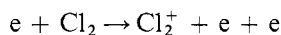
The target-gas atmosphere at a pressure in the range of 10^{-3} – 10^{-1} Pa was prepared by a constant gas-flow method. The gas was introduced into the vacuum vessel within the interaction chamber from a gas handling system through a porous plug, and pumped out by a diffusion pump. The primary gas pressure of the order of $(1\text{--}30) \times 10^2$ Pa inside the gas handling system was measured by a mercury U micrometer manometer.

There are problems with chlorine pressure measurement because it rapidly reacts with the mercury surface. After many unsuccessful attempts it was concluded that the measurement can be done if the mercury surface is first left to react with chlorine so that it becomes covered with a mercury–chlorine layer. This layer protected the rest of the mercury, and pressure measurements of a reasonable quality could be obtained. The relative error of 0.20 in the obtained cross sections is mainly due to the uncertainty of the target-gas pressure.

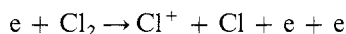
3. Experimental results

With the parallel-plate-type interaction chamber used in our experiment it is not possible to distinguish and separately measure the various ionic species formed in electron–molecule collisions. The measurements were performed by separately collecting all positive or negative ions formed along the electron beam path.

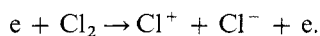
The collection of positive ions gives absolute values for the total ionisation cross sections. Positive ions can be formed in a great number of processes, the most important being molecular ionisation



dissociative ionisation

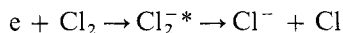


and ion-pair formation

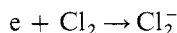


All other processes with the molecular ion, the atom or the ion in excited states are possible as well, and contribute to the total positive-ion signal.

Negative ions can be formed in processes of dissociative attachment



electron attachment



and ion-pair formation. The electron attachment is unlikely to occur in binary electron-molecule collisions. The collection of negative ions gives cross sections for the total negative-ion formation. Since the ion-pair formation process starts at electron energies higher than the lowest positive-ion appearance potential, the collected negative ions for electron energies lower than that give dissociative attachment cross sections only.

3.1. Total ionisation

Total ionisation cross sections were measured in the energy interval between 10 and 100 eV. The energy scale was calibrated within ± 0.08 eV by linearly extrapolating the cross section curve to the 11.48 ± 0.01 eV value for the Cl_2^+ ion appearance potential obtained by Watanabe (1957) by photoionisation. The cross section curve in a range of a few electron volts above the threshold shows breaks, but since the intersection of linearly extrapolated parts of the curve can give only approximate values for higher appearance potentials, we have avoided measuring it. Values of appearance potentials from various authors are scarce and inconsistent. This indicated that further mass-spectrometric investigations by photon and electron impact are needed.

The numerical values of the measured cross sections are listed in table 1. To the authors knowledge, the only other measurement done in the same energy interval is that by Center and Mandl (1972) in which a commercial gas analyser with an incorporated quadrupole filter was used. Their value is higher by 20% than ours at 100 eV, and the curve shows a tendency to rise further, while in our case the maximum was detected at 80 eV.

3.2. Dissociative attachment

As already mentioned, at low electron energies only dissociative attachment processes can take place. The measured cross section curve is shown in figure 1. The energy scale for negative-ion collection was calibrated within ± 0.08 eV to the appearance potential of negative ions from the ion-pair formation process at 11.87 eV. This value was obtained using 13.01 eV for the ionisation potential (Kuhn 1964) and 3.617 eV for the electron affinity of the chlorine atom (Popp 1968), and 2.475 eV for the dissociation energy of the chlorine molecule (Herzberg 1950). The energy scale was cross checked by two other potential values. One was the Cl_2^+ appearance potential at 11.48 eV, and the other the O^- from O_2 dissociation attachment maximum at 6.70 eV. The three energy scales agreed to within 0.05 eV.

Four attachment maxima were found in our experiment, as already reported by Kurepa and Belić (1977).

Table 1. Total ionisation cross sections of the chlorine molecule by electron impact. Units of 10^{-20} m². Relative error ± 0.20 .

Electron energy (eV)	Cross section	Electron energy (eV)	Cross section
11.0	0	20	2.12
11.2	0.016	21	2.38
11.4	0.028	22	2.56
11.6	0.050	23	2.79
11.8	0.068	24	2.97
12.0	0.0927	25	3.18
12.2	0.122	26	3.30
12.4	0.146	27	3.51
12.6	0.158	28	3.66
12.8	0.192	29	3.79
13.0	0.231	30	3.90
13.2	0.283	32	4.09
13.4	0.317	34	4.27
13.6	0.371	36	4.42
13.8	0.414	38	4.53
14.0	0.463	40	4.61
14.2	0.521	42	4.68
14.4	0.581	44	4.80
14.6	0.631	46	4.87
14.8	0.682	48	4.98
15.0	0.747	50	5.06
15.2	0.797	52	5.13
15.4	0.859	54	5.20
15.6	0.913	56	5.26
15.8	0.979	58	5.32
16.0	1.03	60	5.39
16.2	1.09	62	5.43
16.4	1.15	64	5.468
16.6	1.21	66	5.48
16.8	1.26	68	5.52
17.0	1.32	70	5.53
17.2	1.38	72	5.54
17.4	1.43	74	5.56
17.6	1.48	76	5.57
17.8	1.54	78	5.58
18.0	1.59	80	5.58
18.2	1.64	82	5.58
18.4	1.70	84	5.58
18.6	1.75	86	5.58
18.8	1.80	88	5.572
19.0	1.86	90	5.568
19.2	1.91	92	5.56
19.4	1.95	94	5.55
19.6	2.00	96	5.54
19.8	2.07	98	5.535
		100	5.524

The process at zero incident electron energy has the largest cross section. Using special calibration procedures it was proved that at all maxima, including that at zero energy, the normalised negative-ion currents (I_i/I_e) are linear functions of the target-gas pressure, i.e. that they are binary collision events. The cross section value

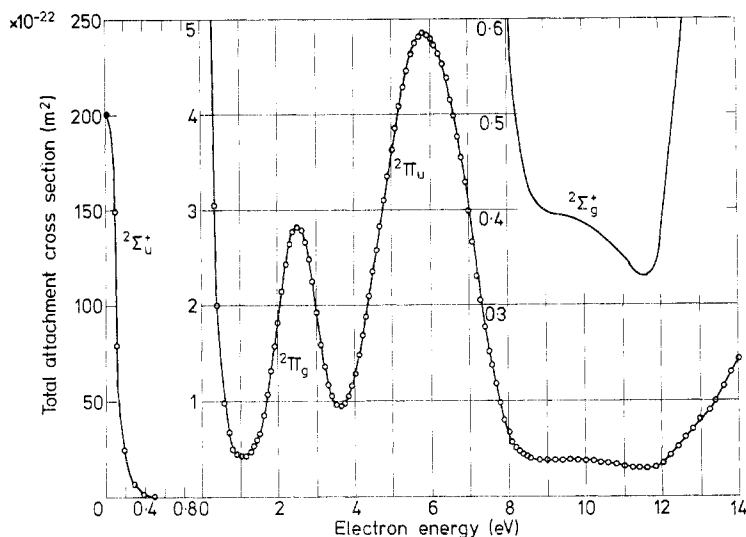


Figure 1. Total electron-attachment cross section of the chlorine molecule in the energy region between 0 and 12 eV.

at zero electron energy depends on the tuning of the trochoidal electron monochromator, a behaviour already detected with the SF_6 molecule (Stamatović 1968). The value of $(201.6 \pm 100) \times 10^{-22} \text{ m}^2$ can thus be questioned in a similar way to the case with the zero energy attachment in SF_6 . In experiments we found that the position of the low energy peak position shifts as a function of the experimental conditions, presumably due to the contact potential changes. But the energy difference between the first and second or third peak, as well as the ion-pair onset remained constant. This makes us believe that when the ion-pair appearance potential is set to the calculated value, the position of all peaks, including the first one is correct.

The existence of a very low energy process was suggested by Schulters *et al* (1975) and Sides *et al* (1976) in order to explain the flowing afterglow experiments in chlorine. The dissociative electron-attachment rate constant of Sides *et al* (1976) for an electron temperature of 350 K, at which their experiments were carried out, gives for the average attachment cross section a value of $(256 \pm 118) \times 10^{-22} \text{ m}^2$, which is in good agreement with our data.

Recent investigations of the Cl_2^- ion ground state by Gilbert and Wahl (1971) and Tasker *et al* (1976) yielded, for the internuclear distance, the values of 2.56 and $2.71 \times 10^{-10} \text{ m}$, respectively. The Morse curve, calculated with the r_e value of Gilbert and Wahl and the dissociation energy of the Cl_2^- ion into Cl^- and Cl of 1.21 eV (Hubers *et al* 1976) crosses the Cl_2 ($^1\Sigma_g^+$) ground state very close to the equilibrium internuclear distance (see figure 2). For this particular position of the potential curves a dissociative attachment process should appear at zero incident electron energy. The large negative-ion peak detected in the energy region close to zero is a proof that the calculated curves closely follow the potentials of the two states involved.

The peak of the second electron-attachment process is at $2.50 \pm 0.08 \text{ eV}$, with a cross section value of $(2.84 \pm 0.56) \times 10^{-22} \text{ m}^2$. The existence of an attachment process in this energy region was found by Thorburn (1959) and Frost and McDowell (1960). In both these measurements the mass spectrometers used were of a lower

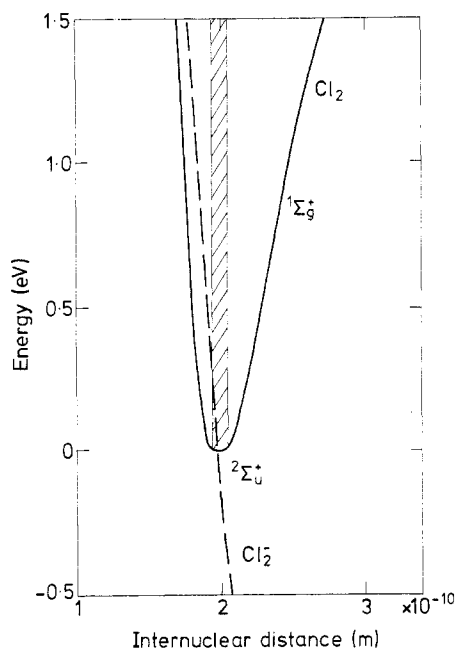


Figure 2. Details of the chlorine molecule ground state ($^1\Sigma_g^+$) and the Cl_2^- ion ground state ($^2\Sigma_g^-$) potential curves showing their crossing.

overall sensitivity than that in our experiment. This might be the reason that the appearance potential of Frost and McDowell is at 0.60 eV higher than our value of $1.0 \pm 0.1 \text{ eV}$, while the position of the maximum is at the same place. In our view, at these electron energies the excited $^2\Pi_g$ repulsive state of the Cl_2^- ion is formed.

The third maximum is at $5.75 \pm 0.08 \text{ eV}$, with an appearance potential of $3.4 \pm 0.1 \text{ eV}$ and a cross section of $(4.84 \pm 0.96) \times 10^{-22} \text{ m}^2$. Thorburn (1959) detected the appearance of negative ions at $4.4 \pm 0.2 \text{ eV}$, while Frost and McDowell (1960) reported their not being able to trace the existence of negative ions in this interval of electron energies. This attachment process we assume to be due to the formation of the $^2\Pi_u$ excited repulsive states of the Cl_2^- ion.

Finally, a fourth process was found at incident electron energies between 9 and 12 eV. It can hardly be distinguished from the tail of the third process, so that both the appearance potential and the position of the maximum could be determined but only with a large error. We suggest a value for the appearance potential of $8.2 \pm 0.3 \text{ eV}$, and for the peak position $9.7 \pm 0.2 \text{ eV}$. At these energies a highly excited $^2\Sigma_g^+$ state of the Cl_2^- ion is formed.

In order to check whether in the processes with maxima at 2.50 and 5.75 eV the excited molecular negative ions formed dissociate into Cl and Cl^- with a limit at 1.14 eV below the ground state of the Cl_2 molecule, a crude energy analysis using a repulsive negative potential to the collector electrode was applied to negative ions. The plot of the relative ion-current intensity, for a given incident electron energy, as a function of the retarding potential extrapolated to the electron energy axis gives the maximum kinetic energy of the ion. The total kinetic energy E_k of the negative Cl^- ion and the neutral Cl atom is related to the incident electron energy E_0 , electron

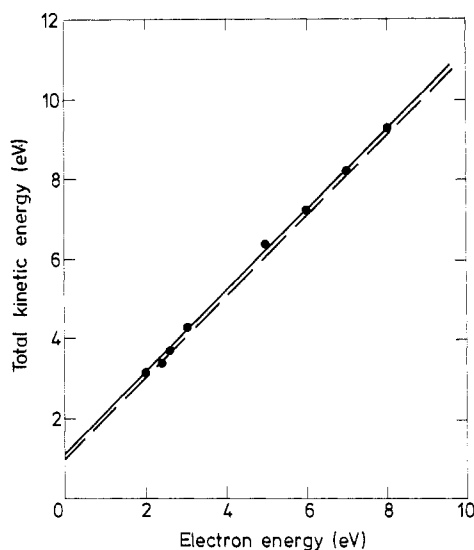


Figure 3. Experimentally obtained total kinetic energies of the Cl and Cl⁻ pair against the incident electron energy. The two lines are calculated for the chlorine atom in its ground (full curve) and excited (broken curve) state, respectively.

affinity EA and the dissociation energy DE of the Cl₂ molecule and the excitation energy E_{ex} of the Cl atom by

$$E_k = [E_0 + \text{EA}(\text{Cl}_2) - \text{DE}(\text{Cl}_2) + E_{\text{ex}}(\text{Cl})]/2.$$

The extrapolated total kinetic energies are plotted in figure 3 as a function of the incident electron energy. Two lines are drawn, corresponding to the calculated kinetic energies of the ion-neutral pair with the Cl atom in the ground (²P_{3/2}) and excited (²P_{1/2}) states, respectively, taking E_{ex} (of ²P_{1/2}) to be 0.109 eV (Candler 1964).

The values of appearance potentials and positions of the peaks are listed in table 2 and compared with data from the literature.

The total electron-attachment cross section values at 0.2 eV intervals are listed in table 3, as well as the partial cross sections for attachments into the ²Σ_u⁺ ground state, and ²Π_g, ²Π_u and ²Σ_g⁺ excited states of the Cl₂⁻ ion. These partial attachment cross sections were obtained by analysing the total cross section curve. The values

Table 2. Appearance potentials of negative ions and positions of peaks from electron attachment to the chlorine molecule.

Process	Appearance potential (eV)	Position of the peak (eV)	Authors
Cl ₂ (² Σ _g ⁻) + e → Cl ₂ ⁻ * (² Σ _u ⁺)	0.0	0.0	This work
Cl ₂ (¹ Σ _g ⁺) + e → Cl ₂ ⁻ * (² Π _g)	1.0 ± 0.1 1.60 ± 0.05 < 2	2.50 ± 0.08 2.5 —	This work Frost and McDowell (1960) Thorburn (1959)
Cl ₂ (¹ Σ _g ⁺) + e → Cl ₂ ⁻ * (² Π _u)	3.4 ± 0.1 4.4 ± 0.2	5.75 ± 0.08 —	This work Thorburn (1959)
Cl ₂ (¹ Σ _g ⁺) + e → Cl ₂ ⁻ * (² Σ _g ⁺)	8.2 ± 0.3	9.7 ± 0.2	This work

Table 3. Total and partial dissociative attachment cross sections of the chlorine molecule. Units of 10^{-22} m^2 . Relative error 0.20.

Electron energy (eV)	Cross section			
	Total	$^2\Sigma_u^+$	$^2\Pi_g$	$^2\Sigma_g^-$
0.0	201.6	201.6		
0.1	80.0	80.0		
0.2	24.5	24.5		
0.3	6.2	6.2		
0.4	2.0	2.0		
0.5	0.98	0.98		
0.6	0.68	0.68		
0.7	0.63	0.63		
0.8	0.50	0.50		
0.9	0.44	0.40	0.04	
1.0	0.42	0.32	0.10	
1.2	0.48	0.14	0.34	
1.4	0.59	0.04	0.53	
1.6	0.84		0.84	
1.8	1.32		1.32	
2.0	1.81		1.81	
2.2	2.42		2.42	
2.4	2.77		2.77	
2.6	2.79		2.79	
2.8	2.49		2.49	
3.0	1.92		1.92	
3.2	1.36		1.36	
3.4	1.06		0.93	0.13
3.6	0.95		0.59	0.36
3.8	1.05		0.36	0.69
4.0	1.29		0.13	1.16
4.2	1.69		0.10	1.59
4.4	2.09			2.09
4.6	2.57			2.57
4.8	3.08			3.08
5.0	3.63			3.63
5.2	4.08			4.08
5.4	4.46			4.46
5.6	4.74			4.74
5.8	4.84			4.84
6.0	4.78			4.78
6.2	4.62			4.62
6.4	4.38			4.38
6.6	3.99			3.99
6.8	3.55			3.55
7.0	3.01			3.01
7.2	2.31			2.31
7.4	1.78			1.78
7.6	1.38			1.38
7.8	1.00			1.00
8.0	0.699			0.699
8.2	0.51			0.48
8.4	0.45			0.33
8.6	0.41			0.22
8.8	0.395			0.12
9.0	0.395			0.05
9.2	0.380			0.01
				0.275
				0.345
				0.370

Table 3. (continued)

Electron energy (eV)	Cross section			
	Total	$^2\Sigma_u^+$	$^2\Pi_g$	$^2\Sigma_u^-$
9.4	0.386			0.386
9.6	0.392			0.392
9.8	0.390			0.390
10.0	0.380			0.380
10.2	0.372			0.372
10.4	0.365			0.365
10.6	0.355			0.355
10.8	0.348			0.348
11.0	0.344			0.344
11.2	0.325			0.325
11.4	0.316			0.316
11.6	0.318			0.290
11.8	0.328			0.270
12.0	0.365			0.245
12.2	0.440			0.220
12.4	0.530			0.170
12.6	0.625			0.130
12.8	0.720			0.095
13.0	0.510			0.050

of the first process are to be taken only as an estimate with a possible relative error as big as 0.50.

3.3. Ion-pair formation

The cross section curve for negative-ion formation at electron energies between 11 and 100 eV is shown in figure 4. Ions in this region can be formed via dissociative

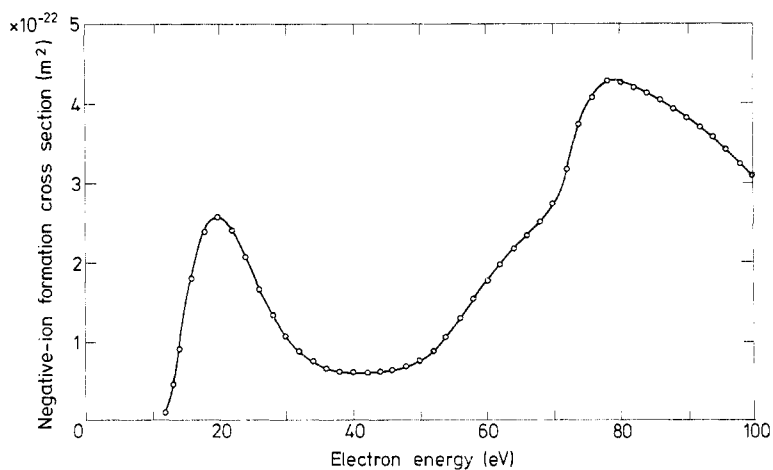


Figure 4. Total cross section curve for negative-ion formation processes in chlorine at energies between 11 and 100 eV.

Table 4. Negative-ion formation cross sections. Units of 10^{-22} m². Relative error 0.20.

Electron energy (eV)	Cross section	Electron energy (eV)	Cross section
12	0.122	60	1.76
13	0.460	62	1.96
14	0.900	64	2.18
16	1.80	66	2.34
18	2.40	68	2.52
20	2.58	70	2.72
22	2.40	72	3.18
24	2.07	74	3.73
26	1.66	76	4.06
28	1.35	78	4.24
30	1.08	79	4.28
32	0.89		
34	0.74	80	4.25
36	0.65	82	4.20
38	0.62	84	4.13
40	0.60	86	4.04
42	0.40	88	3.94
44	0.62	90	3.82
46	0.64	92	3.70
48	0.69	94	3.57
50	0.76	96	3.40
52	0.88	98	3.22
54	1.05	100	3.07
56	1.28		
58	1.52		

attachment processes into highly excited states of the Cl_2^- ion or dissociation processes of the Cl_2 molecule into an ion pair: Cl^+ and Cl^- .

The ion-pair formation process with the Cl^+ ion in its ground state starts at an electron energy of 11.87 eV. The sudden change in the negative-ion curve in figure 1 shows clearly the beginning of this process.

The shape of the negative-ion curve in the region between 11 and 30 eV (figure 4), and the sign of a new onset visible in figure 1 close to the electron energy of 13.3 eV, has led us to believe that a dissociative attachment process dominates in this region, exceeding in magnitude the pair-formation process cross section.

At incident electron energies higher than 40 eV the negative-ion formation curve shows new features. A slow rise between 40 and 46 eV is followed by a series of peaks at about 46, 52 and 70 eV. The next maximum of the curve lies at 79 eV.

The numerical values of negative-ion formation cross sections are listed in table 4.

Acknowledgment

Thanks are due to T L Gilbert of ANL, USA for valuable comments on the assignment of Cl_2^- negative states to which the attachment of electrons takes place.

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