Electron Attachment and Ionization in Oxygen, Carbon Monoxide and Carbon Dioxide

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Abstract. Electron attachment and ionization cross section measurements have been made under single collision conditions both by an absolute and a comparative method, and are compared with recent relevant data. The corrections employed in the latter are seen to be valid in view of the good agreement with the absolute measurements. In the absolute measurements a Tate and Smith type apparatus is used where all the ions are collected and the measurements do not involve any kinetic energy or angular discriminations. Ionization cross sections for 80 ev electrons in the three gases oxygen, carbon monoxide and carbon dioxide are 2.76×10^{-16} cm², 2.93×10^{-16} cm² and 4.23×10^{-16} cm² respectively, while the peak resonance attachment cross sections resulting in the formation of O⁻ are 1.32×10^{-18} cm², 2.18×10^{-19} cm², 1.37×10^{-19} cm² and 4.44×10^{-19} cm² at 6.7, 10.1, 4.45 and 8.15 ev respectively. The value 1.37×10^{-19} cm² at 4.45 ev corresponds to a second peak observed in carbon dioxide. Ionization potentials corresponding to the formation of positive ions and the onset potentials corresponding to the formation of negative ions in the dissociative process have been determined.

§1. INTRODUCTION

IONIZATION and attachment cross section measurements are reported in this paper to resolve the discrepancies in the existing data in oxygen. Two values of peak resonance attachment cross sections in this gas are reported in the literature. Craggs, Thorburn and Tozer (1957) give a value of $(2.25 \pm 0.3) \times 10^{-18}$ cm², while Buchelnikova (1953) gives a value of $(1.3 \pm 0.2) \times 10^{-18}$ cm². The cross section curves given in these two papers have been used by Prasad and Craggs (1960) to evaluate mean attachment cross sections as a function of mean electron energy and to compare with similar values derived from swarm data. These authors find that the cross section measurements of Buchelnikova show better agreement with swarm data if a Druyvesteyn form of distribution is assumed. Since there is no justification for assuming this distribution, the agreement does not provide conclusive proof regarding the validity of the attachment efficiency curve obtained by Buchelnikova, although later American work provides further confirmation.

In the ionization efficiency curve in oxygen Craggs *et al.* find that they differ from the measurement of Tate and Smith (1932) at low electron energies after normalizing their oxygen cross section to that of Tate and Smith at 40 ev. The discrepancy is explained as being due to the increase in electron path length in the experiments of Tate and Smith at low electron energies on the basis of the formula given by Massey and Burhop (1952, p. 34). This matter is discussed later in the paper.

Precise absolute ionization and attachment cross section measurements are therefore only possible in an apparatus where the various parameters are such that the increase in

path length as derived from the above formula is negligible even at low electron accelerating voltages.

In view of these discrepancies in oxygen it was felt desirable to redetermine ionization and attachment cross sections in that gas and in carbon monoxide and carbon dioxide, for which at that time only the data of Craggs and Tozer (1958, 1960) existed, with the exception of ionization cross sections in carbon monoxide (Tate and Smith 1932) and two isolated values of ionization cross sections in carbon dioxide at 75 ev by Otvos and Stevenson (1956) and Lampe *et al.* (1957). However, at the time of writing this paper measurements of attachment and ionization cross sections in oxygen, carbon monoxide and carbon dioxide were published by Schulz (1962). It is seen that the measurements of Schulz in general show better agreement with our present data. The cross section measurements of Craggs *et al.* and Schulz are comparative, but the present data, however, also include a set of absolute measurements.†

Measurement of the onset potentials for ionization and attachment in the three gases have been made on an absolute energy scale. The method of establishing the absolute scale has been described by Asundi and Kurepa (1963).

§ 2. EXPERIMENTAL DETAILS

The results reported in this paper have been obtained in two types of apparatus. One of them is of the Lozier pattern (L) with which only comparative cross section measurements are possible, and the other is of a type due to Tate and Smith (TS) with which absolute cross section measurements have been made. In both of them a beam of electrons, obtained from a hot tungsten filament, is accelerated through a system of circular apertures to the desired energy and enters a chamber where it interacts with the gas under investigation at a pressure of about 10^{-4} to 10^{-5} mmHg, and is finally collected on the electron collector. The electron beam is collimated by an axial magnetic field (of about 150 oersteds), which also helps to keep the electrons from reaching the ion collector situated in the chamber. The ions formed are drawn out by the ion collector plate (TS) or the cylindrical collector (L) with the appropriate potential. The essential difference between the L and the TS apparatus is that in the latter all the ions formed within the length of the collector plate are collected, whereas in the former only a fraction of the ions formed are collected. Further details of the two apparatus can be found in the literature (Lozier 1934, Marriott and Craggs 1954, E. R. A. Technical Report L/T308, Tate and Smith 1932).

† The reasons for carrying out similar experiments simultaneously with an absolute and a comparative method are as follows.

The comparative (Lozier) method has been used for many years in this Laboratory primarily for the purpose of measuring the kinetic energy of the fragmentary products of ionization of molecules by electron impact. We later developed a method of measuring ionization and attachment cross sections, but it was always necessary to refer the data to some absolute standard such as the work of Tate and Smith (1932). However, this apparatus was in recent years modified to take an RPD electron gun of the kind first developed by Fox and his collaborators in the Westinghouse Laboratories and has given some useful results, so that it was felt worth while to continue with it. At the same time, however, it was realized some six years or so ago that an absolute apparatus was clearly necessary, and at that time we began work with the modified Tate and Smith apparatus of the present communication. Experimental details of this technique will it is hoped be published elsewhere by Downey and Craggs.

The comparison of results taken with these two forms of apparatus shows that, for example, the peculiar collection system of the Lozier apparatus does not appear to have any energy discrimination over the range of electron velocities described in this paper.

Preliminary experiments were made to establish the linear dependence of ion current against electron current and ion current against gas pressure and that all the electrons and ions (TS) are collected.

§3. CROSS SECTION MEASUREMENTS

The ionization and attachment cross section measurements with the TS apparatus have been computed from the following formula:

$$Q = \frac{i_\pm}{i_e} \frac{T}{273} LP \times 3 \cdot 56 \times 10^{16}$$

where $i_\pm$ is the positive or negative ion current, i_e is the electron current, T is the absolute temperature in °K, P is the sample pressure in mmHg and L is the length of the ion collector in cm.

The basis of the cross section measurements in the L apparatus is the comparison of the ion yields in a standard and the sample under investigation at normalized electron current and gas pressure. Thus, where i and I are the ion currents for the sample and the standard at the respective electron energies, $Q(S)_e$ is the cross section of the standard and $Q(X)_E$ that of the sample for electrons of energy e and E respectively, then

$$Q(X)_E = Q(S)_e i/I.$$

Positive ion cross sections have been obtained by comparing the positive ion currents in the three gases with that produced in argon at 80 ev and employing for argon the cross section given by Smith (1930) for this energy. Attachment cross sections have been obtained by independent comparison with both positive ion and negative ion yields in the parent and other gases.

The errors in ionization cross section measurements are ± 7%. The main contribution to the error arises from errors in pressure measurements. A McLeod gauge has been used in the TS apparatus while a Knudsen gauge has been used in the L apparatus. The attachment cross sections determined from measurements made in the L apparatus, however, are likely to have errors slightly greater than 7% since the evaluation involves a correction factor depending on the kinetic energy of the negative ion and is only approximate. The agreement between these results and the absolute values obtained by us (TS) is, however, to within ± 10%.

The electron energy scale has been corrected by an absolute method based on the shift of the maxima in the electron energy distributions derived by the retarding potential method. The scale thus established is accurate to within ± 0·01 ev (Asundi and Kurepa 1963).

§4. RESULTS AND DISCUSSION

4.1. *Positive Ions*

Tables 1, 2 and 3 give the ionization cross section for electron energies in the range corresponding to the ionization potential up to 80 ev in oxygen, carbon monoxide and carbon dioxide. The tables compare the present relative and absolute measurements made by the authors with the data in the literature.

Oxygen. In oxygen the agreement with Tate and Smith's (1932) values in the entire energy region measured is seen to be good, while cross sections reported by Craggs, Thorburn and Tozer (1957), standardized at 40 ev with the value obtained by Tate and Smith (1932), are considerably lower for energies up to 20 ev. This discrepancy between their results and those of Tate and Smith has been attributed to the increase in

the electron path length by Craggs *et al.* They find that on the basis of the formula given by Massey and Burhop a variation of 28% in the maximum electron path length for electron energies of 40 ev and 20 ev in the original Tate and Smith experiments is to be expected. In both the present sets of apparatus this variation is found to be less than 3%. Hence, in view of the good agreement observed between our results and those of Tate and Smith, it appears that there is no increase in the electron path in the Tate and Smith experiments even though they have used considerably larger apertures compared with those of all other authors. At 20 ev the present measurements agree with those of Tate and Smith to within ±3%. Similar agreement has been observed by Fite and Brackmann (1959) and Schulz (1962). The measurements by Craggs *et al.* are 23% less at this energy.

Table 1

Ionization Cross Section in Oxygen O_2

$(10^{-16}$ cm$^2)$

ev	Tate & Smith (1932)	Craggs et al. (1957)	Schulz (1962)	Present Relative	Present Absolute
13	0·014	—	—	0·04	0 028
14	0·06	0,02	0 07	0·08	0 058
15	—	—	—	0·12	0 086
16	0·16	0,08	0 16	0·16	0 128
17	—	—	—	0·22	0 17
18	0·25	0·15	0 27	0·28	0 23
19	—	—	—	0·33	0 33
20	0·41	0,31	0 41	0·40	0 40
22	—	—	—	—	0 53
24	—	—	—	0·78	—
25	0·79	0.68	0 78		0 79
26	—	—	—	—	0 86
28	—	—	—		1 00
30	1 18	1,17	1 20	1 14	1·11
35	1·55	1.55	1·55	1·53	1 48
40	1 84	1.84	—	1·78	1·73
45	2·03	—	—	2·00	1·99
50	2·20	—	—	2 20	2 18
55	2 34	—	—	2·36	2 29
60	2·46	—	—	2·47	2·44
65	2·55	—	—	2·60	2 57
70	2 63	—	—	2·64	2 66
75	2·70	—	—	2·70	2 73
80	2·76	—	—	2·76	2 77
85	—	—	—	—	2 76
90	—	—	—	—	2 76
95	—	—	—	—	—
100	—	—	—		

Table 2

Ionization Cross Sections in Carbon Monoxide
(in units of 10^{-16} cm²)

ev	Tate & Smith (1932)	Craggs & Tozer (1958)	Schulz (1962)	Present Relative	Present Absolute
15	—	—	—	—	0·056
16	0 11	0·13	0 12	0·13	0 12
17	—	—	—	—	0·21
18	0 26	0·37	0 27	0 32	0·31
19	—	—	—	—	0·40
20	0 41	0·60	0'47	0·55	0·49
22	—	—	—	—	0·66
24	—	—	—	—	0·84
25	0·97	1·21	0 91	1·09	0·93
26	—	—	—	—	1·12
28	—	—	—	—	1·22
35	1·78	2·22	1·66	1 95	1·88
40	2·11	2·51	2·00	2 20	2 05
45	—	—	—	—	2·25
50	2·54	2 82	2·42	2 50	2·42
55	—	—	—	—	2·60
60	2·77	2 96	2·73	2 70	2·72
65	—	—	—	—	2·82
70	2·93	3·02	2·94	2 80	2·88
75	—	—	—	—	2·93
80	3·03	3 03	3·13	2 90	2·96
85	—	—	—	—	2·98
90	—	—	—	—	3·00
95	—	—	—	—	3·06
100	—	3 07	3·07	—	3 06

Carbon monoxide. Reference to table 2 shows that the cross section values obtained by Tate and Smith (1932) in carbon monoxide agree within experimental errors with present measurements above 20 ev. In the energy region up to 20 ev slightly larger values are observed (15%). In the threshold to 20 ev region our results lie between the two sets of measurements reported, namely those of Tate and Smith and Craggs and Tozer (1958). Even though measurements by Fox (1961) are available in this region showing agreement with Tate and Smith, it is not certain that the latter results are accurate since Fox normalizes ion current in this gas to the cross section given by Tate and Smith at 20 ev. The discrepancies near the threshold could be in part due to errors in the calibration of the energy scale.

Carbon dioxide. The ionization cross sections observed in carbon dioxide are considerably lower than those observed by Craggs and Tozer (1960) in the entire electron energy range. The two other cross section values reported in the literature corresponding to an electron energy of 75 ev are $3·46 \times 10^{-16}$ cm² by Otvos and Stevenson (1956) and $4·31 \times 10^{-16}$ cm² by Lampe *et al.* (1957). These are not absolute measurements, but those of Lampe *et al.* compare favourably with present data. The value obtained by Craggs and Tozer for this energy is nearly 65% higher.

Table 3

Ionization Cross Sections in Carbon Dioxide
(in units of 10^{-16} cm²)

ev	Craggs & Tozer (1960)	Present Relative	Absolute
15	0·18	0 13	0 14
16	0·36	0 24	0·26
17	0·55	0·35	0·37
18	0·75	0·50	0·50
19	0·95	—	0 64
20	1·16	0·73	0 77
22	1·60	1·00	1 07
24	2·05	1·28	1 35
25	2·26	—	1 48
26	2·50	1·57	1 63
28	2·92	1·86	1 90
30	3·30	2·10	2 16
35	3·94	2·50	2 59
40	4·38	2·80	2 97
45	4·78	3 10	3·20
50	5·10	3·30	3 42
55	5·40	3·60	3·72
60	5·68	3 70	3·95
65	5·96	3·8	4 04
70	6·22	3·9	4 13
75	6·44	4 0	4 28
80	6·68	4 0	4·43
85	6·80	4·0	4 40
90	6·76	4·1	4·45
95	6·76	4·1	4 42
100	—	—	4 38

4.2. Negative Ions

Oxygen. Cross section values corresponding to the maxima of the resonant attachment peak and the electron energy corresponding to its onset and maxima are given in table 7, while detailed cross section values of the resonant attachment peak are given in tables 4, 5 and 6.

The peak resonant cross section value for oxygen observed in the present experiments ($1·34 \pm 0·1 \times 10^{-18}$ cm²) supports the value obtained by Buchelnikova (1953) and the recent value reported by Schulz (1962). Craggs *et al.* observe that the apparent attachment cross section is pressure and electron current dependent. Since the highest pressure employed by these authors is lower than the pressure required for the single-collision condition, the pressure effect is difficult to explain although these authors invoked scattering effects. Further, in a Lozier type apparatus the collection efficiency of the collector is dependent on the kinetic energy of the ion collected (Tozer 1958). This was corrected by Craggs *et al.* by using appropriate potentials in the inverse ratio of the
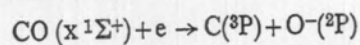
Table 4

Attachment Cross Sections in Oxygen O_2
(in units of 10^{-19} cm²)

ev	Buchelnikova (1953)	Schulz (1962)	Present Relative	Present Absolute
4·0	—	—	—	0·27
4·2	—	—	—	0·44
4·4	—	—	—	0·70
4·6	—	—	0·75	1·17
4·8	—	0·20	1·10	1·80
5·0	0·20	0·50	1·90	2·62
	0·50	0·78	3·20	3·99
	1·30	1·30	4·20	5·65
	3·40	2·6	6·50	7·53
	5·30	3·1	8·50	9·01
6·0	7·00	4·5	10·2	10·7
	9·00	6·5	12·1	11·8
	11·2	10·4	13·0	12·8
	12·7	11·6	13·0	13·1
	13·0	12·7	12·6	13·3
7·0	13·1	12·9	11·3	13·3
	12·7	12·5	9·50	12·8
	11·18	11·6	8·20	12·1
	9·50	10·4	6·40	11·2
	8·00	8·84	5·00	9·24
8·0	6·50	7·54	3·90	7·01
	4·80	6·00	2·65	4·75
	3·90	4·8	1·90	2·97
	—	3·6	1·45	1·90
	—	2·7	1·05	1·76
9·0	—	2·0	0·75	1·34
	—	1·56	0·50	1·10
	—	1·30	0·35	0·79
	—	1·04	0·20	0·78
	—	0·65	0·10	0·70
10·0	—	0·62	—	0·64

kinetic energy of the ion. This introduced a further correction while collecting high kinetic energy ions owing to the small collecting potential employed in the presence of the magnetic field. However, in the present experiments a collecting potential sufficient to overcome the magnetic field is used in all cases and the collection efficiencies are normalized using a correction factor which has been evaluated. The large cross section observed by Craggs *et al.* could be due to some of the reasons mentioned above.

Carbon monoxide. The attachment process

$$CO\ (x\ {}^1\Sigma^+) + e \rightarrow C({}^3P) + O^-({}^2P)$$

observed has a peak resonance attachment cross section of $(2·18 \pm 0·2) \times 10^{-19}$ cm².

Table 5

Attachment Cross Sections in Carbon Monoxide
(in units of 10^{-19} cm^2)

ev	Relative	Present Absolute	ev	Relative	Present Absolute
8·0	—	—	11 0	0 82	1 27
	0·32	—		—	0 98
	—	—		0 49	0 71
	0·21	0·040		—	0 50
	—	0·080		0·25	0 34
9·0	0·19	0·120	12 0	—	0·23
	0·20	0·18		0 16	0 15
	0·41	0·40		—	0 10
	0·82	0·83		—	0 07
	1·61	1·48		—	0 05
10 0	2·06	2·14	13·0	—	0 04
	1·98	2·36			
	1·69	2·19			
	1·36	1 88			
	1 08	1·63			

Table 6

Attachment Cross Sections in Carbon Dioxide
(in units of 10^{-19} cm^2)

| ev	Schulz (1962)	Present Relative	Present Absolute	ev	Schulz (1962)	Present Relative	Present Absolute
3·0	—	—	0 02	7·0	0 55	0 74	1 21
	—	—	0 04		1·20	1 12	1 78
	—	0·04	0 10		1·85	1 56	2 44
	—	0·13	0·21		2 60	2·28	3 24
	0·05	0·30	0 47		3 45	3 04	3 99
4 0	0·20	0 66	0 90	8·0	4·25	3·76	4 33
	0·70	1·24	1·32		4·40	4 50	4 12
	1·25	1·28	1·52		3·60	4 48	3 16
	1 50	1·08	1 31		2 30	3 60	2 00
	1 35	0·80	0 90		1 20	2·50	1 16
5 0	0 85	0·34	0 52	9·0	0·75	1·40	0 83
	0·50	0 08	0 28		0·55	0·80	0 46
	0 20	0 00	0 20		0 40	0·50	0 33
	0 10	0 00	0 16		0·20	0 32	0 22
	0 00	0 00	0 18		0·10	0 18	0 17
6·0	0 00	0 00	0 23	10 0	—	0 06	0 15
	0 00	0 01	0 29				
	0 05	0·14	0 40				
	0 15	0 30	0 56				
	0 35	0 50	0 84				

This favours the Craggs and Tozer (1958) measurement, while the estimate of Massey $(5 \times 10^{-20}$ cm^2) is seen to be far too low. A better agreement between the present values and the measurements of Craggs and Tozer is obtained if the present attachment cross section in oxygen and the ionization cross section in carbon monoxide are used to evaluate the attachment cross section in carbon monoxide. This yields a cross section of $2 \cdot 0 \times 10^{-19}$ cm^2. The attachment curve in carbon monoxide obtained from the L apparatus showed some negative current in the energy range 5·5 to 8·5 ev which was not present in the measurements made in the TS apparatus. This is probably due to meta-stable molecules hitting the vanes and releasing secondary electrons in the L apparatus, as explained by Schulz (1962).

Carbon dioxide. The electron attachment cross section in carbon dioxide as a function of electron energy is shown in the figure. An attachment peak in addition to the one
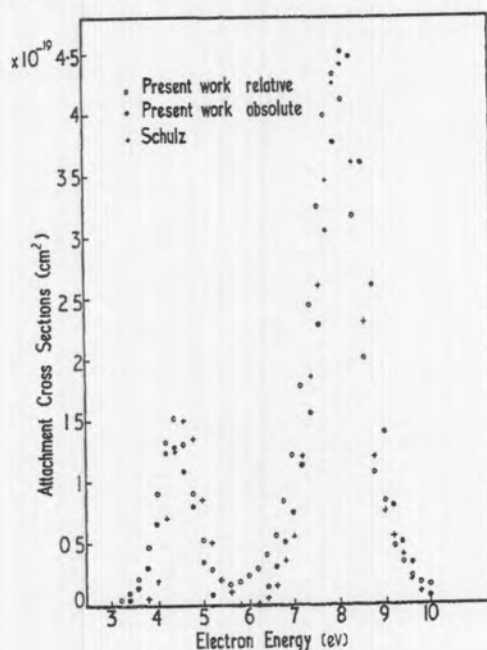
reported by Craggs and Tozer (1960) is observed. The new peak which appears at lower electron energies has a maximum cross section which is about a third of the second peak. This peak has also been observed by Schulz (1962). The two attachment peaks are believed to be due to the dissociative capture process

$$CO_2 + e \rightarrow CO(x\ ^1\Sigma^+) + O^-(^2P).$$
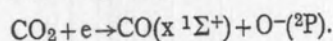
The two processes differ only in the kinetic energies involved. The present peak resonance cross section for the larger peak is again found to be slightly lower than the value obtained by Craggs and Tozer. The agreement in the cross section values reported by Schulz are seen to be good for both peaks.

4.3. Onset Potentials

The onset potentials of positive ions have been evaluated on an absolute energy scale, established with an accuracy to $\pm 0 \cdot 08$ ev by a method reported in our earlier