ELECTRON TRANSFER AND REACTIVE IONIZATION IN C + O_2 COLLISIONS IN THE ELECTRON VOLT ENERGY RANGE

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Cross sections for ion formation in C + O_2 collisions have been measured as a function of the kinetic energy up to 15 eV. Charge transfer is found to give rise to C^+, O_2^-, C^-, O_2^+ and free electrons. Five processes leading to these ions have been identified. Reactive ionization is taking place, proceeding according to three processes: C + O_2 → CO^+ + O + e^-, CO^+ + O^- and CO + O^+ + e^-.

1. Introduction

The development of atomic beam sources in the electron volt region about six years ago has led to an extensive study of charge transfer processes in atom–molecule collisions [1–3]. The various aspects of alkali-halogen charge transfer processes have especially been the subject of investigation. Relatively unexplored however, are atom–molecule collisions in which no alkalis or halogens are involved. These systems are of interest since in these instances ionization requires a close approach of the colliding particles, and reactive ionization is frequently observed [3–5].

Among the many possible collisional ionization experiments with non-alkalis which can be done, the system C + O_2 (see table 1) is of particular interest. Wexler [3], who studied angular distributions of positive ions formed in collisions of sputtered C atoms with O_2 molecules (however, without velocity selection of the C beam), found that both C^+ and O_2^+ ions are formed. This indicates that in C + O_2 collisions two competing charge exchange processes are occurring, a feature that has never been observed before in any other system.

In this letter we report measurements on the various processes which take place in C + O_2 collisions as a function of energy up to 15 eV. It will be shown that besides the charge transfer processes various reactive ionization processes occur.

Table 1
Ionization potentials (IP), electron affinities (EA) and dissociation energies E_{diss} of some C and O containing atoms and molecules. Values are expressed in eV

	IP [11]	EA	$E_{diss}(25°)$ [11]
C	11.26	1.27 [17]	–
O	13.61	1.47 [11]	–
O_2	12.06	0.43 [16]	5.16
CO	14.01	−1.75 [18]	11.14
C_2	12.0	3.54 [12]	6.25

2. Experimental

2.1. The apparatus

The apparatus has been described previously [6]. Particles are sputtered from a polycrystalline carbon target by a 6 keV Ar^+ ion beam, and after velocity selection and collimation crossed with a thermal oxygen beam. Charged particles formed in the C + O_2 collisions are accelerated in an electric field of 400 V/cm, pass a magnetic spectrometer and are counted on a particle multiplier. In order to reach the high velocities required for the present experiment, a larger velocity spread than usual was applied on the selector. The velocity selector was calibrated using aniline (An) as target gas, measuring

$Cl + An \rightarrow Cl^- + An^+ - 4.08$ eV [7], which has a linear energy dependence of the ionization cross section. The resolution $\Delta v/v$ of the selector was determined to be 15%.

2.2. Carbon beams obtained by sputtering

The energy distribution dS/dE of sputtered C atoms from polycrystalline targets is not yet known experimentally. In general however, after mechanical velocity selection, the flow of sputtered atoms is proportional to $E\,(dS/dE) \propto E^2/(E + E_b)^{n+1}$, in which E is the kinetic energy of the atoms, E_b the binding energy of the atom on the lattice (E_b = 7.4 eV for C [8]) and n is a constant between 1.5 and 2 [6,9,10]. Since this function varies only about 15% for C in the energy range in which the present experiments are done, the counting rates on the multiplier are considered to be proportional to the ionization cross sections.

It is to be expected that C_2 molecules (dissociation energy 6.25 eV [11]) and excited C atoms are also sputtered from the target. Indeed, crossing sputtered beams from C or WC targets with An, strong signals were observed from the process $C_2 + An \rightarrow C_2^- + An^+$; crossing the sputtered beam with oxygen however, no trace of C_2^- or C_2^+ molecules was detected. Obviously, the ionization cross sections for $C_2 + O_2$ are negligible compared to $C + O_2$. Therefore in the interpretation of the data of the following sections the presence of C_2 is not considered.

C has two long lived excited states at low energies, the ^1D and the ^1S state, lying respectively 1.26 and 2.68 eV above the ^3P ground state [13]. One might expect that part of the sputtered C atoms are in this state. However, no shifts were observed in the thresholds of ions formed in $C + O_2$ collisions, which may be due to the presence of excited atoms. It is not clear if the ionization cross sections for these atoms are indeed so low, or that the excited atom is quenched before the ionizing collision takes place. A third explanation may be that the singlet states are simply not sputtered. A similar effect has been observed in neutralization of He^+ on Cu surfaces [14], in which only the triplet He states are populated.

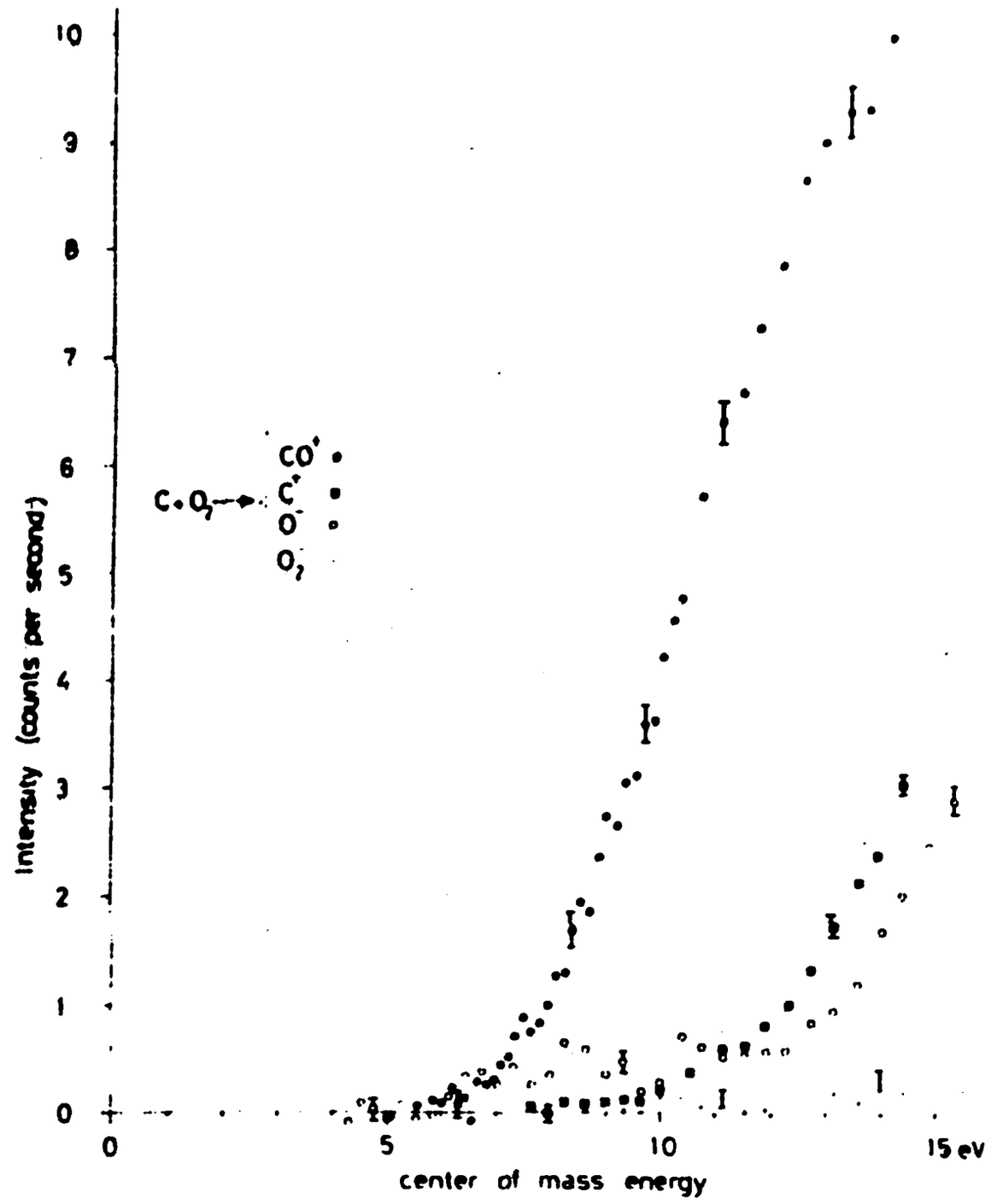

Fig. 1. Production of C^+, CO^+, O^- and O_2^- ions in $C + O_2$ collisions as a function of the $C - O_2$ c.m. energy. The y axis represents the multiplier current in counts per second, which is in a good approximation proportional to the cross section (see section 2.2). For some experimental points, the statistical uncertainty has been indicated.

3. Results

In figs. 1 and 2 the intensities of the ions formed in $C + O_2$ collisions are given as a function of energy. As has been mentioned before, the y axis is about proportional to the cross sections. Apart from the species C^+ and O_2^+, which are reported by Wexler [3], also C^-, O^+, O^-, O_2^- and CO^+ ions are observed. From figs. 1 and 2 it can be seen that the cross section for formation of positive ions is much higher than for formation of negative ions. This implies that also a considerable amount of free electrons is produced in $C + O_2$ collisions. In our system however, electrons cannot be detected directly. Table 2 gives the relative intensities of all detected ions with a non-selected beam, and at 14.2 eV, together with the threshold energies. The relative intensities are accurate within 10%. Most thresholds were

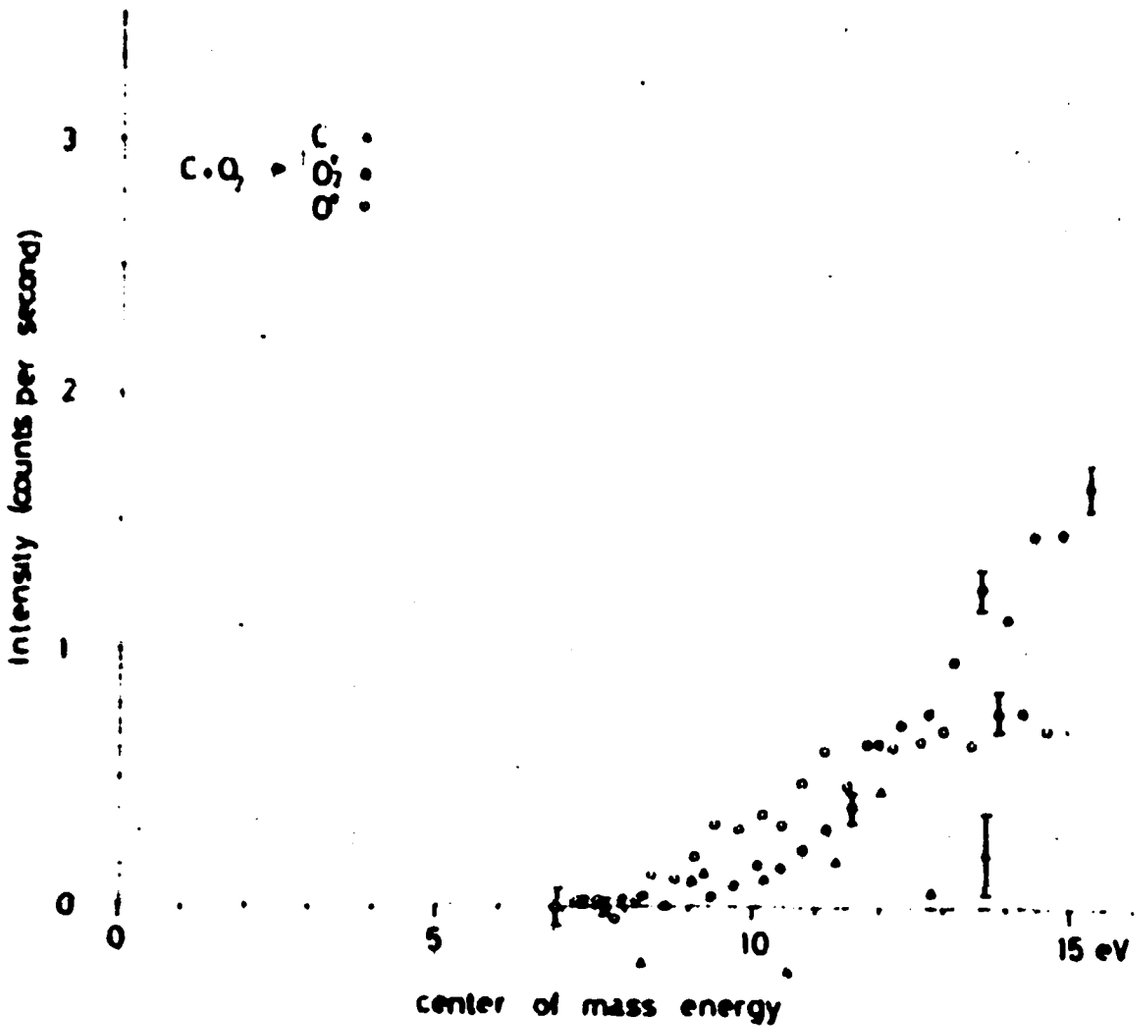

Fig. 2. Production of C^-, O^+ and O_2^+ ions in C + O_2 collisions as a function of the C – O_2 c.m. energy. The y axis represents the multiplier current in counts per second, which is in a good approximation proportional to the cross section (see section 2.2). For some experimental points, the statistical uncertainty has been indicated.

determined by fitting the experimental results with a linear model cross section (LF) which is convoluted with the resolution function of the velocity selector, as described previously [7]. The O^- curve however, gave no fit; here a step function model (SF) was used. The sharp increase at high energy in the O^- curve may reflect the onset of a new process. Its threshold was calculated by subtracting the signal at lower energies and fitting with the SF procedure. The thresholds for C^- and O_2^- production were not determined by fitting with a model cross section, since the signal to noise ratio of the experimental points is rather poor. Here, only a rough estimate is given (*RE*).

From the density of the O_2 beam and an estimate of the C beam flow we calculate that a signal of 10 c/s at the multiplier collector corresponds to a cross section in the order of 0.2 –0.5 $Å^2$.

Table 2
Relative intensities of the observed ions in C + O_2 collisions, with non-selected beams and at 14.2 eV c.m. energy. E_{thr} is the experimental threshold energy for the ions. LF and SF are thresholds found by fitting with a linear and a step function model, RE are rough estimates (see text)

	Intensity unselected	Intensity 14.2 eV	E_{thr}(eV)
C^+	100	26	11.2 ± 0.2 (LF)
O^+	22	8	7.9 ± 0.3 (LF)
CO^+	45	100	7.9 ± 0.2 (LF)
O_2^+	38	13	10.6 ± 0.2 (LF)
C^-	13	3	11 ± 1 (RE)
O^-	52	18	6.5 ± 0.3 (SF)
			15.1 ± 0.3 (SF)
O_2^-	10	2.5	10.5 ± 1 (RE)

4. Discussion

The charged products can be divided into two groups. Referring to the charge of the C ion, they will be called the *positive channel* and the *negative channel*. The positive channel leads to C^+, O^-, O_2^- and CO^+ formation, the negative channel to C^-, O^+ and O_2^+. Fig. 1 thus represents the positive channel and fig. 2 the negative channel. From these figures and from table 2 it follows that the negative channel has a considerably lower cross section than the positive channel. Table 3 gives the threshold energies for charge transfer and reactive ionization in both channels, calculated from the data of table 1. In this section we will discuss both channels separately and identify the processes occurring in C + O_2 collision with the aid of the tables and figures.

Table 3
Calculated threshold energies for ionization processes in C + O_2 collisions

	Positive channel		Negative channel		
	C + O_2 →	E_{thr}(eV)	C + O_2 →	E_{thr}(eV)	
c1	$C^+ + O_2^-$	10.83	$C^- + O_2^+$	10.79	charge
c2	$C^+ + O_2 + e^-$	11.26	$C + O_2^+ + e^-$	12.06	transfer
c3	$C^+ + O^- + O$	14.95	$C^- + O^+ + O$	17.50	
r1	$CO^+ + O^-$	6.56	$CO^- + O^+$	9.38	reactive
r2	$CO^+ + O + e^-$	8.03	$CO + O^+ + e^-$	7.63	ionization

4.1. The positive channel

As can be seen in fig. 1, the first peaks which appear in the positive channel are CO^+ and O^-. Up to about 7 eV these signals have equal intensity. This implies that these ions originate from reaction r1 in table 3, $C + O_2 \rightarrow CO^+ + O^-$. Indeed, the threshold for O^- formation (table 2) agrees within the experimental error with the calculated threshold for $CO^+ + O^-$ formation as given in table 3. At higher energies, the CO^+ signal rises higher than the O^-. Apparently in this energy region, the reaction r2 ($C + O_2 \rightarrow CO^+ + O + e^-$) also takes place. At higher energies the cross section for r2 is much larger than for r1. The threshold for CO^+ formation, found by linear extrapolation (table 2) is mainly determined by process r2, and agrees within the experimental error with the theoretical value in table 3. If the O^- signal is subtracted from the CO^+ signal, the LF threshold of the resulting CO^+ curve becomes about 8.0 eV, and is thus in agreement with its theoretical value for process r2.

Above 10 eV, also C^+ and O_2^- ions are formed. The O_2^- formation must be due to the charge transfer process c1, $C + O_2 \rightarrow C^+ + O_2^-$. The C^+ signal however rises much faster than the O_2^- indicating that C^+ ions are dominantly formed in process c2, $C + O_2 \rightarrow C^+ + O_2 + e^-$. The threshold for C^+ in table 2 agrees with the theoretical value of this latter process. Finally, O^- shows a sharp increase at 13 eV. Of course, this effect may be due to an increase of the $CO^+ + O^-$ cross section. However, a fit of this increasing signal with the SF model yields a threshold of 15.1 eV (see table 2), which agrees within the experimental error with the theoretical value of process c3 giving $C^+ + O^- + O$. We therefore have the impression that this latter process is responsible for the increase of the O^- signal at high energies. Summarizing, it can be concluded that all processes r1, r2, c1, c2, c3 contribute to ion formation in the positive channel.

As can be seen from fig. 1, the O_2^- signal is very low compared to C^+. The whole C^+ curve however can be fitted with the LF model, yielding the threshold for the process $C + O_2 \rightarrow C^+ + O_2 + e^-$, and not for the energetically more favorable process $C + O_2 \rightarrow C^+ + O_2^-$, as can be seen from tables 2 and 3. This indicates that the "real" C^+ curve (measured with an ideal velocity selector with infinite resolution) behaves as follows: it has a low value between the $C^+ + O_2^-$ and $C^+ + O_2 + e^-$ thresholds and shows a sharp linear increase if this latter process becomes energetically possible. This behaviour is completely different from $K + O_2$ collisions, in which no such increase in the total charge transfer cross section is observed at the $K^+ + O_2 + e^-$ threshold [15]. This is due to the fact that in this system the colliding particles separate as $K^+ + O_2^-$, after which free electrons may be formed by autoionization of vibrationally excited O_2^- ions. Therefore the charge transfer cross section reflects only the behaviour of $K^+ + O_2^-$ formation, since this autoionization is a secondary process. The sharp increase in the C^+ curve on the other hand indicates, that in the present case the electrons are formed before the colliding particles separate as C^+ and O_2^-, thus if these particles are close together. On the contrary, at the energy where the channel $C^+ + O^- + O$ is opened, no extra increase in the C^+ curve is observed: the whole C^+ curve can be fitted with the LF model for $C^+ + O_2 + e^-$ formation. This means that the process $C + O_2 \rightarrow C^+ + O + O^-$ is related to $C^+ + O_2 + e^-$ formation, since O^- formation apparently occurs at the cost of electron formation.

The differences in behaviour in the charge transfer processes in $C + O_2$ and $K + O_2$ collisions can be understood as follows. In $C + O_2$ collisions, ionization requires a much closer approach of the colliding particles than in $K + O_2$, since the thresholds are much higher. Whereas the O_2^- formation can be described by Franck–Condon transitions in the O_2 potential curves in $K + O_2$ formation, this is no longer possible for $C + O_2$. It is known that C has a very strong chemical attraction to O_2. From the fact that reactive ionization has a large cross section in this system, it can be concluded that these attractive forces play a very dominant role in $C + O_2$ collisions. This means that these collisions have to be described on the whole system of potential hypersurfaces of the CO_2 pseudomolecule as a three-body problem. The processes $C + O_2 \rightarrow C^+ + O_2^-$ and $C^+ + O_2 + e^-$ apparently describe very different paths on these hypersurfaces, which leads to the observed behaviour of the C^+ cross section curve.

The CO^+ threshold in table 2 agrees with the process $C + O_2 \rightarrow CO^+ + O + e^-$. The weak O^- signal on the other hand reflects the process $C + O_2 \rightarrow CO^+ + O^-$. Apparently, the "real" CO^+ curve behaves like C^+: a low cross section between both thresholds and a steep rise above the second one. This indicates that free electron formation does not occur after the separation of CO^+ and O^- ions by autoionization of the O^- ion. Clearly also in this

case the free electron is formed when the colliding particles are close together. In this picture it is interesting that the $C + O_2 \rightarrow CO^+ + O^-$ cross section is hardly energy dependent, while the $C + O_2 \rightarrow CO^+ + O + e^-$ cross section shows a dramatic increase with energy in fig. 1.

As can be seen from table 2 and fig. 1, the cross section for CO^+ formation at 14.2 eV is about a factor of four higher than for C^+. In unselected beams however, the CO^+ signal is only fifty percent of the C^+ signal. This indicates that at very high energies the CO^+ cross section will become lower than the C^+ cross section. It is indeed to be expected that at high energies reactive ionization will have a small cross section, since the probability for rearrangement will be lower if the collision time is decreased.

No signal could be detected of the associative ionization process $C + O_2 \rightarrow CO_2^+ + e^- - 2.28$ eV. This is in contrast to the systems U, Ti, Ce, Ba + O_2 in which associative ionization has been observed [3–5].

4.2. The negative channel

In the negative channel, C^-, O^+ and O_2^+ ions are formed. Since the O_2^+ threshold lies below 11 eV, the process e1 ($C + O_2 \rightarrow C^- + O_2^+$) apparently contributes to the negative channel. From the experimental O_2^+ threshold we find an electron affinity of 1.5 eV for C atoms, which is in agreement with the value given in table 1.

As can be seen from fig. 2, the C^- signal is much lower than the O_2^+ signal for higher energies. This indicates that there is a considerable contribution of the process e2 ($C + O_2 \rightarrow C + O_2^+ + e^-$) in the negative channel. In contrast to the processes e1 and e2 in the positive channel, in this case the O_2^+ curve can be fitted with the LF model of the energetically most favourable process $C + O_2 \rightarrow C^- + O_2^+$. This indicates that the process e2 proceeds as follows: $C + O_2 \rightarrow C^- + O_2^+ \rightarrow C + O_2^+ + e^-$.

As can be seen from fig. 2, O^+ ions are formed far below the threshold at 17.5 eV of process e3, giving $C^- + O^+ + O$. The experimental threshold for O^+ is even lower than for O_2^+. This can only be explained if O^+ ions are formed in one of the reactive ionization processes r1 or r2. From these two possibilities the $C + O_2 \rightarrow CO^- + O^+$ threshold is significantly higher than the experimental O^+ threshold. Therefore O^+ must be formed in the process r2: $C + O_2 \rightarrow CO + O^+ + e^-$. It can however not be excluded that at higher energies the process $C + O_2 \rightarrow CO^- + O^+$ also contributes to O^+ formation. CO^- ions are unstable and autionize in a short time. Therefore they can never be detected on the multiplier.

Up to now, $C + O_2$ is the only system in which ionization in both the positive and negative channel is observed. Wexler [3] who only observed the C^+ and O_2^+ ions, assumed that these products are formed in both charge exchange processes e1 giving $C^+ + O_2^-$ and $C^- + O_2^+$ respectively. He suggested that the existence of both processes e1 is due to the low difference in the thresholds (10.83 eV and 10.79 eV respectively).

Our measurements indicate that C^+ is mainly formed in the process $C + O_2 \rightarrow C^+ + O_2 + e^-$. This does not mean however, that Wexler's argument is invalid. In fact, if the first step in the collision is a promotion of the system to the $C^+O_2^-$ or $C^-O_2^+$ hypersurface, after which electron loss or rearrangement takes place, Wexler's explanation can still be applied. It is not impossible, however, that for the positive channel in which reactive ionization is so dominant, the first step is CO + O formation, after which ionization takes place. If this is the case, the existence of both channels might be correlated with the strong chemical interactions in the C–O_2 system. It would be interesting to see if a system like Si–O_2, in which the three body interactions are expected to be analogous to C–O_2, also gives ionization in both channels.

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