Measurement of Electron Attachment Coefficient in Oxygen and Oxygen-Argon Mixtures

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We analyzed the electron arrival time signal measured in pure oxygen and in dilute oxygen-argon mixtures by using a double shutter electron drift tube with variable drift distance and derived the density normalized attachment coefficient for respective gases. The present attachment coefficient determined for pure oxygen agreed well with previously reported values and we confirmed that the present apparatus was useful in determining electron attachment coefficient even if there were no ionization, when there will be no steady state current growth and, hence, the steady state Townsend (SST) method can not be applied in principle. The measured attachment coefficients in the mixtures agreed very well with the calculation using our latest cross section set for the oxygen molecule and that will be a confirmation for the validity of the cross section set.

Key Words: Oxygen, Oxygen-argon mixtures, Three-body attachment, Two-body attachment, The density normalized electron attachment coefficient

1. Introduction

Oxygen is probably one of the most thoroughly studied molecules among other electro-negative gas molecules. And its electron attachment has been attracting attentions of many investigators.

Bradbury(1) determined the probability of electron attachment in oxygen and its mixtures with nitrogen, argon, and helium. Chanin et al.(2) measured the attachment coefficient in pure oxygen and in oxygen-helium mixtures as a function of E/N and determined the two-body and the three-body attachment coefficients of oxygen at various gas pressures at two different temperatures.

Aleksandrov(3) studied theoretically three-body electron attachment to the oxygen molecule using the Bloch-Bradbury mechanism. Phelps(4) compiled a set of electron collision cross sections of the oxygen molecule basically from electron transport data measured in pure oxygen.

We also have been measuring the drift velocity and the longitudinal diffusion coefficient in dilute oxygen-argon mixtures and in pure oxygen in order to determine an accurate set of electron collision cross sections for the oxygen molecule in lower electron energy range. The transport coefficients were measured by using a double shutter electron drift tube with variable drift distance and the measured arrival time distributions sometimes showed appreciable electron loss, possibly due to electron attachment, in low E/N both in the mixtures and in pure oxygen. This electron loss, in one hand, disturbed our measurement but it, on the other hand, may possibly provide a new method for the measurement of electron attachment coefficients.

In the present study, we analyzed the measured arrival time distributions and tried to derive the electron attachment coefficient from them.

2. Experimental Procedure

The apparatus, a double shutter electron drift tube, used in the present measurement was described in detail previously(5) and its details will not be given here, but it should be noted here that its drift distance was variable from 1 to 10 cm and the arrival time distribution of electron pulse emitted at the first shutter was recorded at several drift distances, typically 2-10 cm when measurements were possible. A typical example of the arrival time distributions...
(ATD) measured in pure oxygen \((E/N = 50 \text{Td}, N = 3.535 \times 10^{16} \text{cm}^{-3})\) is shown in figure 1. During the measurement the bias voltage and the shutter pulse height to each shutter were unaltered in order to keep the electron transmission through the shutter constant, and we assumed the area under each distribution was directly proportional to the electron number \(n\) arriving at the second shutter. Estimated diffusion length by using the transverse diffusion coefficient from our Boltzmann analysis was typically less than 2.5 cm in \(10 < E/N < 100 \text{Td}\).

This result can be compared with the inner radius of the present apparatus (=5 cm) and we, therefore, neglected the transverse diffusion loss of electrons in the present measurement.

![Figure 1](image1.png)

**Figure 1.** An example for arrival time distributions of electrons measured in pure oxygen. \((E/N = 50 \text{Td}, N = 3.535 \times 10^{16} \text{cm}^{-3})\)

![Figure 2](image2.png)

**Figure 2.** The normalized area of the arrival distributions as a function of the distance \((E/N = 50 \text{Td}, N = 3.535 \times 10^{16} \text{cm}^{-3})\).

The semi-logarithmic plot of the normalized area, or \(\log(n/n_0)\), where \(n_0\) is the number of electrons arriving at the second shutter at the minimum drift distance, against the drift distance show good linearity as shown in figure 2 and we determined the attachment coefficient from the slope of the linear plot. In the low \(E/N\) in the present study, we can apparently disregard the ionization by electron collisions. That was also confirmed by the Boltzmann equation analysis separately.

The density normalized attachment coefficient, \(\eta /N\), was measured in pure oxygen and in the 1.01% and 4.994% oxygen-argon mixtures. The mixtures were composed of pure oxygen (99.99% purity) and argon (99.9999% purity) and the actual mix ratio was determined by using a gas chromatography test.

All measurements were carried out at room temperature, 300 ± 2K.

The range of the present measurements was summarized in Table 1.

**Table 1. Summary of range of measurements**

<table>
<thead>
<tr>
<th>Gas</th>
<th>E/N</th>
<th>Range of gas number density</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.01%</td>
<td>0.03-2 Td</td>
<td>(7.07 \times 10^{17} - 3.535 \times 10^{16} \text{cm}^{-3}) ((2.67-133 \text{kPa}))</td>
</tr>
<tr>
<td>4.994%</td>
<td>0.12-3 Td</td>
<td>(1.061 \times 10^{18} - 7.071 \times 10^{17} \text{cm}^{-3}) ((4.00-26.7 \text{kPa}))</td>
</tr>
<tr>
<td>Pure</td>
<td>1.7-100 Td</td>
<td>(7.07 \times 10^{17} - 7.071 \times 10^{16} \text{cm}^{-3}) ((0.0267-2.67 \text{kPa}))</td>
</tr>
</tbody>
</table>

Accuracy of the present attachment coefficient was mainly determined by the stability of the electrometer and the error limit for the experimental results was hard to specify, but typical scatters of the measured values at different pressures at each \(E/N\) was less than 12% except for over the \(E/N\) range where three-body attachment process was appreciable.

3. Experimental Results

3.1 Attachment coefficient in pure oxygen

The result of the attachment coefficient, \(\eta /N\), measured in pure oxygen at different gas number densities in higher \(E/N\) \((E/N > 10 \text{Td})\) by solid symbols as well as other published results of different authors\(^{(2,6-10)}\) by open symbols were
summarized in figure 3.

The present result shows no apparent gas number density dependence and agrees very well with those published values shown in the figure. The curves in the figure show the results of the Boltzmann equation analysis (see the following section).

Figure 3. The density normalized electron attachment coefficients, $\eta /N$, as a function of $E/N$ being two-body attachment processes in pure oxygen.

The present attachment coefficient measured in low $E/N$ ($E/N < 8$ Td), on the other hand, showed a sharp dependence on the gas number density and increased linearly as the gas number density increased at each $E/N$. Typical arrival time distributions observed at different gas number densities in this $E/N$ range ($E/N = 4$ Td, $N = 28.28$, $35.35$ and $70.70 \times 10^{16}$ cm$^{-3}$, respectively) are compared in figure 4.

Apparently the attenuation of the electron number arriving at the second shutter with increasing the drift distance is more obvious at higher gas number density. Figure 4 may give impression that the mean arrival time of electrons depends on the gas number density, but the delay time in the figure actually was measured from the starting time of the second shutter pulse which can be set arbitrary in the measurement at each gas number density. The electron drift velocity and the $N_{DL}$ can also be determined from the mean arrival time and the characteristic width of the distribution, respectively, and the effects of the attenuation seen in the figure on these transport coefficients were small and were well within the estimated error limits described in the previous section.

The semi-logarithmic plots of the normalized area of the arrival distributions against the drift distance for the ATDs shown in figure 4 are shown in figure 5. The slope of these linear plots gives the attachment coefficient, $\eta /N$, and the figure actually shows the density dependence of the coefficient.

Figure 5. The normalized area of the arrival distributions as a function of the distance for three difference gas number density ($E/N = 4$ Td).

The density dependence of the present $\eta /N$ by solid symbols and that measured by Chanin $et$ $al.$(2) by open symbols in pure oxygen in lower $E/N$ ($E/N \leq 10$ Td) are shown in figure 6.

Figure 7 shows that the logarithmic plot of these results shown in figure 6 against the gas number density at $E/N = 4$ Td lies along the single line with the slope of 1 and agreement of the two results was
confirmed.
This linear dependence of the coefficient on the gas number density clearly indicates that the working attachment process in this E/N range is three-body process.

![Figure 6. The density normalized electron attachment coefficients, η/N, as a function of E/N being three-body attachment processes in pure oxygen and in oxygen-argon mixtures.](image1)

The foregoing results and discussions confirmed that the arrival time distributions observed in the present double shutter electron drift tube can be used to determine the electron attachment coefficients as well as the drift velocity and the NDL of electrons. The attachment coefficient was actually measured in very low E/N where the ionization by electron collisions are negligible. The SST method has been conveniently used to determine the ionization and attachment coefficients which relies on the current growth equation. The current growth equation, however, becomes \( I(d) = I_0 \) in the limit of \( \alpha \ll \eta \), where \( I_0 \) is the initial electron current released from the cathode and \( d \) the electrode separation, and the SST method will not be practical to determine the attachment coefficient in this limiting case.

3.2 Attachment coefficient in the oxygen-argon mixtures

In the oxygen-argon mixtures the measured arrival time distribution showed the similar but weaker attenuation. The present η/N in both mixtures are shown in figure 6 by respective solid and open symbols and compared with that in pure oxygen.

![Figure 7. The comparison of the density normalized electron attachment coefficients, η/N, as a function of the product of the gas number density and the drift distance at 4 Td.](image2)

The measured attachment coefficients at higher E/N (E/N ≥ 1 Td) in both mixtures in several gas number densities are summarized in figure 8. They are fairly smaller than in pure oxygen and do not
show any appreciable density dependence. The attachment process in the mixtures in this E/N range is therefore two-body process. It increases as E/N increase increases in the present measurement but we had to give up the measurement in E/N > 3 Td because of the deteriorated function of the shutter in the higher E/N. The reason for the deteriorated shutter function was not clear but confined effects of electron attachment and the shutter structure of the present apparatus may account for it. The present shutter was specially designed for higher electron transmission in lower E/N and inherently has weaker performance to electrons with higher energies.

The curves in figure 8 show the results of the Boltzmann equation analysis as in figure 3.

There were no other measurement on attachment coefficient in oxygen-argon mixtures to compare with the present result. In intermediate E/N range, 0.2 ≤ E/N < 1 Td in 1.01% mixture and 0.5 < E/N < 1.4 Td in 4.994% mixture, the attachment coefficient was too small to determine by the experiment.

In low E/N, where attachment is three-body, the measured η /N was higher in the mixture with higher oxygen concentration and, on the other hand, the opposite was the case in higher E/N, where attachment is two-body. In low E/N the electron energy distribution is nearly thermal and electron attachment rate is determined nearly by the oxygen concentration. But the two-body attachment process has its threshold (4.9 eV) and the electron energy distribution in the mixture with higher oxygen concentration tends to be confined in lower energy range because of higher inelastic energy loss rate. And, therefore, the η /N in the 4.994% oxygen-argon mixture is lower than in the 1.01% oxygen-argon mixture in E/N > 1 Td.

4. Boltzmann Equation Analysis

The density normalized attachment and ionization coefficients in pure oxygen and the 1.01% and 4.994% oxygen-argon mixtures were analyzed by using a two-term Boltzmann equation analysis. The cross section set for the argon atom determined by Nakamura and Kurachi{11} was used throughout the present study. The set of cross sections for the oxygen molecule used in the present study was also determined by us in order that the set was able to reproduce the drift velocity and the ND in the oxygen-argon mixtures and in pure oxygen as well as the ionization and attachment coefficients in pure oxygen. The validity of the two-term approximation for the analysis of the electron transport coefficients in pure oxygen and the mixtures was confirmed by comparing the results by the two-term approximation with those by the Monte Carlo calculation at several E/N using the same sets of cross sections for argon and oxygen. Neither computer code of the present calculations includes the three-body attachment process and the results were compared only with the measured attachment coefficients of two-body process. The calculated attachment coefficient in pure oxygen was shown in figure 3 by the dotted curve and those in the 1.01% and 4.994% mixtures are shown by the solid and dotted curves in figure 8, and agreement with the measurement was fairly well. The present cross section set for oxygen naturally can give the consistent attachment coefficient in pure oxygen, but it is also confirmed that the present cross section can reproduce the attachment coefficients measured in the present oxygen-argon mixtures fairly well. This fact is an additional confirmation of the validity of our latest cross section set for the oxygen molecule.

5. Conclusion

We analyzed the arrival time distributions of electron measured in pure oxygen and in the 1.01% and 4.994% oxygen-argon mixtures by using a double shutter drift tube with variable drift distance (1-10 cm) and derived the density normalized electron attachment coefficient for respective gases. The present attachment coefficient determined in pure oxygen agreed well with the previously reported values and we confirmed that the present apparatus was useful in determining electron attachment coefficient even if there were no ionization, when there will be no steady state current growth and, hence, the SST method can not be applied to determine the attachment coefficient in principle. The measured attachment coefficients in the mixtures agreed very well with the calculation using our latest cross section set for the oxygen
molecule and that will be a confirmation for the validity of the cross section set.

(Received 28 November 1997, revised manuscript received 4 March 1998)

Reference


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