Measurement of Electron Impact Ionisation and Attachment Coefficients in NO2/He Gas Mixtures and Estimated Electron Collision Cross Sections for NO2

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Abstract
The electron impact ionisation $\alpha/p_0$ and attachment coefficients $\eta/p_0$ in NO2/He gas mixtures, where $p_0$ is the gas pressure at 0°C, are measured by a steady-state Townsend method over a wide range of compositions and $E/p_0$ values. Based on the experimental values of $\alpha/p_0$ and $\eta/p_0$, a preliminary set of the cross sections for NO2 is estimated by a Boltzmann equation analysis and values of the cross sections are discussed.

1. Introduction
Nitrogen dioxide (NO2) is one of the most difficult air pollutants to remove chemically. Therefore, a number of attempts to decompose NO2 in exhaust gases by corona discharges have been carried out recently (e.g. Masuda and Nakao 1990). The NO2 molecules in glow discharges are shown to decompose into N2 and O2 (Sakai and Tagashira 1993). In order to develop non-equilibrium plasma technologies for pollution control, further basic data such as chemical reaction rates, electron swarm parameters and electron collision cross sections for NO2 are necessary. The reaction rates among electrons, NO2 molecules and their products have recently been reviewed (Alekseev et al. 1993). Various kinds of negative ion such as NO2-, O2-, NO- and O- in NO2 gas discharges have been observed (Abouaf et al. 1976) and the electron impact ionisation and attachment coefficients in NO2/air mixtures have been measured (Okumura et al. 1994); however, the electron–NO2 collision cross sections required to understand the mechanism of their formation are not available. Obtaining these data is essential to understand discharges for pollution control.

In this paper, the electron impact ionisation $\alpha/p_0$ and attachment coefficients $\eta/p_0$, where $p_0$ is the gas pressure at 0°C, are measured by a steady-state Townsend method for NO2/He gas mixtures ranging from $K = 0$ to 1, where $K$ is the NO2 mol fraction and $50 < E/p_0 < 300$ V cm$^{-1}$ Torr$^{-1}$ (152 $< E/N < 912$Td). These gases may provide very different values for the ionisation and attachment coefficients in certain $E/p_0$ ranges depending on NO2 mol fractions, since the form of the cross section for NO2 (a molecular gas) is expected to be completely different from that of He (a rare gas). Such gas mixtures should be well suited for

determining cross section values which are not known well, such as NO$_2$, using the Boltzmann equation (BE) method through adjustment of the cross sections so as to obtain the swarm parameters consistent with experimental ones.

Next, based on the measured values of $\alpha$ and $\eta$ presented in this paper and using available cross section data for NO$_2$, a preliminary set of electron collision cross sections for NO$_2$ is estimated by the BE method.

2. Measurement of $\alpha$ and $\eta$ Coefficients

The experimental set-up for the measurement of the ionisation current and the procedure for determination of $\alpha$ and $\eta$ values are the same as described in a previous paper (Okumura et al. 1994). Briefly, brass Harrison profile (Pearson and Harrison 1969) electrodes with a flat area of 110 mm in diameter and coated with a vacuum deposited 40 nm thick gold thin film are installed in the discharge chamber of a stainless-steel cylinder of diameter 300 mm and height 420 mm. The chamber and the gas inlet pipe system are evacuated to about $10^{-6}$ Torr by diffusion and rotary pumps. A gas impurity level of about $3 \times 10^{-3}$ mol% is obtained in 60 minutes at 1 Torr ($\equiv$133 Pa). We used 99.9% purity NO$_2$ and 99.99% purity He gases.

![Diagram](image.png)

**Fig. 1.** Cross sections for He where $Q_m$ is the momentum transfer cross section, $Q_{ex*}$ the excitation cross section to the metastable state, $Q_{ex}$ a grouped cross section to excitation states except the metastable state, and $Q_i$ the ionisation cross section.

3. Procedure for the Coefficient Analysis

The $\alpha$, $\eta$ and secondary ionisation coefficient $\gamma_T$ are evaluated by fitting the measured ionisation current growth $J$ ($10^{-13}$–$10^{-9}$ A) to the following modified Townsend equation using a linearised least-mean-squares technique (Thomas 1966):
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\[
J = J_0 \frac{\alpha \exp((\alpha - \eta)d)/((\alpha - \eta))}{1 - [\alpha \gamma_T/((\alpha - \eta))] \{\exp((\alpha - \eta)d) - 1\}},
\]

where \( J_0 \) is the externally maintained photoelectron current at the cathode. The gap separation \( d \) is increased from 0.1 to 2.3 cm.

The coefficients \( \alpha \) and \( \eta \) determined by this method are accurate to within 6% and 10% respectively, as the total measurement error is evaluated to be about 3%, which arises from errors in the adjustment of the gap distance, the applied voltage, the fluctuation of the UV light intensity, the current measurement, and so on.

\[ Q_m/10 \]
\[ Q_v \]
\[ Q_d \]
\[ Q_i \]
\[ Q_{aq} \]
\[ Q_{ex} \]
\[ Q_{d1} \]
\[ Q_{d2} \]
\[ Q_{ci} \]

**Fig. 2.** Cross sections for NO\(_2\) where \( Q_m \) is the momentum transfer cross section, \( Q_v \) the vibrational excitation cross section, \( Q_{d1} \) and \( Q_{d2} \) the dissociation cross sections for NO\(_2 \rightarrow\) O+NO and NO\(_2 \rightarrow\) N+O\(_2\) respectively, \( Q_a \) the electron attachment cross section, \( Q_{ex} \) a grouped cross section to the excitation states, and \( Q_i \) the ionisation cross section.

### 4. Boltzmann Equation Method

The electron energy distribution used to determine \( \alpha \) and \( \eta \) was calculated by a Boltzmann equation (BE) of the conventional two term approximation (Thomas 1969; Sakai et al. 1979) using the set of the cross sections shown in Figs 1 and 2.

### 5. Electron Collision Cross Sections of He and NO\(_2\)

The cross sections for He adopted in this work are shown in Fig. 1. The cross sections for NO\(_2\) estimated by fitting \( \alpha \) and \( \eta \) values calculated by the BE method to the experimental ones are shown in Fig. 2. For He, the momentum transfer cross section \( Q_m \) is taken from the data of Frost and Phelps (1964).
The excitation cross section to the metastable state $Q_{ex^*}$ is taken from Zetner et al. (1986). The ionisation cross section $Q_i$ used is the experimentally determined values of Montague et al. (1984). The excitation cross section $Q_{ex}$ is an effective one representing a group of excited states.

The cross section for NO$_2$ is discussed in Section 6c.

![Graph](image)

**Fig. 3.** Coefficient $\alpha/p_0$ as a function of $E/p_0$ for experimental values $K = 0$ (He), open circles; 0·1, pluses; 0·2, crosses; 0·3, open squares, 0·4, open triangles; 0·6, closed triangles; 0·8, closed circles; and 1·0 (NO$_2$), solid squares. The curves are the BE analysed values.

### 6. Results and Discussion

#### (6a) Ionisation Coefficient $\alpha/p_0$

Electron impact ionisation coefficients $\alpha/p_0$ in NO$_2$/He gas mixtures as functions of $E/p_0$ and $K$ are shown in Figs 3 and 4 respectively. The symbols are experimental values and the curves are values obtained by a BE analysis using the present set of cross sections. Both values agree well in the present experimental range of $K$ and $E/p_0$. The $\alpha$ value in He gas increases steeply with increasing $E/p_0$ for low $E/p_0$ values and shows a tendency to saturate for large $E/p_0$. In NO$_2$ gas, however, $\alpha/p_0$ rises slowly at low $E/p_0$ and for $E/p_0 > 150$ V cm$^{-1}$ Torr$^{-1}$ it is found to increase linearly with $E/p_0$. The value of $E/p_0$ at which $\alpha/p_0$ of He is equal to that of NO$_2$ is around 200 V cm$^{-1}$ Torr$^{-1}$. It is seen in Fig. 4 that the $\alpha/p_0$ value depends significantly on $K$. In He gas the experimental values of $\alpha/p_0$ are larger than those from BE analysis for $E/p_0 < 220$ V cm$^{-1}$ Torr$^{-1}$. This inconsistency might be caused by small impurities in rare gases as indicated by Thomas (1969) or by the set of the cross sections applied in this work. The consistency of values between experimental and BE analysis is better for large $K$ values.
The coefficient $\alpha/p_0$ does not change linearly with $K$ as shown in Fig. 4. For $E/p_0 > 100 \text{ V cm}^{-1} \text{Torr}^{-1}$, a maximum appears in the $\alpha/p_0$ versus $K$ curves. The value of $K$ at which the $\alpha/p_0$ maximum is obtained increases with increasing $E/p_0$. The agreement between measured values and those determined by the BE for large $K$ is very good.

The limiting $E/p_0$ at which $\alpha/p_0 = \eta/p_0$ is 100 V cm$^{-1}$ Torr$^{-1}$ for NO$_2$ (Okumura et al. 1994). In the mixtures, not shown in the present figures, this limiting value decreases from 100 V cm$^{-1}$ Torr$^{-1}$ with decreasing $K$.

(6b) Attachment Coefficient $\eta/p_0$

The electron attachment coefficient $\eta/p_0$ in NO$_2$/He gas mixtures is the largest when $K = 1$ (NO$_2$) and decreases rapidly with increasing $E/p_0$ as shown in Fig. 5. It also increases with increasing $K$ as shown in Fig. 6. In the present pressure range, $\eta/p_0$ does not vary with pressure. As seen in Fig. 5, though the experimental values of $\eta/p_0$ are scattered, in the $E/p_0$ range where the $\eta/p_0$ values are measured they agree reasonably well with the BE values. It is expected that $\eta/p_0$ will increase significantly with decreasing $E/p_0$ for a low $E/p_0$ region, based on the BE result.
(6c) Electron Collision Cross Sections for NO$_2$

The present set of cross sections for NO$_2$ is a preliminary one, since the present $Q_m$ is an estimation based on that for N$_2$O (Ramsauer and Kollath 1930; Brueche 1927) taking account of the total absolute electron scattering cross section (Szmytkowski et al. 1992), because of no available $Q_m$ data for NO$_2$. It is also difficult to estimate reliable $Q_m$ values independently from swarm data, because no data on electron drift velocity are reported. The present absolute value of $Q_m$ is smaller by about a factor of two than the values of $Q_m$ for N$_2$O and the total value of the scattering of NO$_2$.

The molecular weights of NO$_2$ and N$_2$O are quite close: 46 for NO$_2$ and 44 for N$_2$O. However, there are significant differences in molecular configuration: i.e. NO$_2$ has a bend shape and N$_2$O is a linear molecule. The dipole moment of NO$_2$ is larger than the N$_2$O value by a factor of 1.9. So, even if it might not be completely correct to use the $Q_m$ of N$_2$O as a first approximation, the $Q_m$ of N$_2$O (Ramsauer and Kollath 1930; Brueche 1927) was used as a value from which the present $Q_m$ is derived.

For the vibrational cross section $Q_v$, we used the first vibrational levels of 0.16, 0.093 and 0.2 eV (Laborie et al. 1971) and grouped them with a threshold of 0.093 and the maximum of $7\times10^{-17}$ cm$^2$ at 0.15 eV as shown in Fig. 2. The dissociation cross sections with the threshold energies of 3.11 eV for the reaction NO$_2$ $\rightarrow$ O+NO ($Q_{d1}$) and of 4.50 eV for the reaction NO$_2$ $\rightarrow$ N+O$_2$ ($Q_{d2}$) (Laborie et al. 1971) are shown in Fig. 2.
The electron attachment cross section $Q_a$ is estimated from the data of Fox (1960). A threshold of 1.35 eV is used taking into consideration various species of negative ions, NO$_{2}^-$, NO$^-$, O$^-$ and O$_2^-$ (Abouaf et al. 1976). Here, the $Q_a$ value is larger than the Fox value by a factor of 60, so as to obtain a $\eta/p_0$ value consistent with the experimental ones.

The threshold of the effective electronic excitation cross sections $Q_{ex}$ used was 5.0 eV, taking account of several levels (Herzberg 1966). The $Q_{ex}$ value was adjusted as shown in Fig. 2 by comparing the experimental and BE $\alpha$ and $\eta$ values. The ionisation cross section $Q_i$ is also unavailable; however, the threshold energy is reported to be between 9.8 eV (Herzberg 1966) and 11.5 eV (Collin and Lossing 1958). In this work the threshold is taken to be 9.8 eV and the maximum $Q_i$ value is set to be $1.4 \times 10^{-17}$ cm$^2$ at 80 eV.

The values of $\alpha$ and $\eta$ depend strongly on the values of $Q_m$, $Q_1$ and $Q_a$. When we varied these three cross sections by 10%, $\alpha$ and $\eta$ for NO$_2$ changed by more than 20% and it became difficult to obtain consistent $\alpha$ and $\eta$ for the mixtures with the experimental ones.

This is a preliminary set of cross sections for NO$_2$, since few data on the collision cross sections for electrons and electron swarm parameters are available.

7. Conclusion

The electron impact ionisation $\alpha/p_0$ and attachment $\eta/p_0$ coefficients in NO$_2$/He mixtures have been measured by a steady-state Townsend method over a wide range of compositions and $E/p_0$ values. Based on the measured values of $\alpha$ and $\eta$, preliminary cross sections for NO$_2$ have been estimated.
Acknowledgment

We would like to thank Dr P. Ventzek, Mrs H. Sugawara, S. Sawada and H. Akashi in the authors' Laboratory, and Mrs S. Matsuda, Y. Satoh and I. Miyoshi of JR Hokkaido Ltd, for useful discussions and constructing the experimental apparatus.

References


Manuscript received 26 August 1994, accepted 17 March 1995