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Measurement of Electron Impact Ionisation and Attachment Coefficients in NO_2/He Gas Mixtures and Estimated Electron Collision Cross Sections for NO_2*

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Abstract

The electron impact ionisation α/p_0 and attachment coefficients η/p_0 in NO_2/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 α/p_0 and η/p_0, a preliminary set of the cross sections for NO_2 is estimated by a Boltzmann equation analysis and values of the cross sections are discussed.

1. Introduction

Nitrogen dioxide (NO_2) is one of the most difficult air pollutants to remove chemically. Therefore, a number of attempts to decompose NO_2 in exhaust gases by corona discharges have been carried out recently (e.g. Masuda and Nakao 1990). The NO_2 molecules in glow discharges are shown to decompose into N_2 and O_2 (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 NO_2 are necessary. The reaction rates among electrons, NO_2 molecules and their products have recently been reviewed (Alekseev *et al.* 1993). Various kinds of negative ion such as NO_2^-, O_2^-, NO^- and O^- in NO_2 gas discharges have been observed (Abouaf *et al.* 1976) and the electron impact ionisation and attachment coefficients in NO_2/air mixtures have been measured (Okumura *et al.* 1994); however, the electron–NO_2 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 α/p_0 and attachment coefficients η/p_0, where p_0 is the gas pressure at 0°C, are measured by a steady-state Townsend method for NO_2/He gas mixtures ranging from $K = 0$ to 1, where K is the NO_2 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 NO_2 mol fractions, since the form of the cross section for NO_2 (a molecular gas) is expected to be completely different from that of He (a rare gas). Such gas mixtures should be well suited for

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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 α and η 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 α and η Coefficients

The experimental set-up for the measurement of the ionisation current and the procedure for determination of α and η 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 3×10^{-3} mol% is obtained in 60 minutes at 1 Torr (≡133 Pa). We used 99·9% purity NO_2 and 99·99% purity He gases.

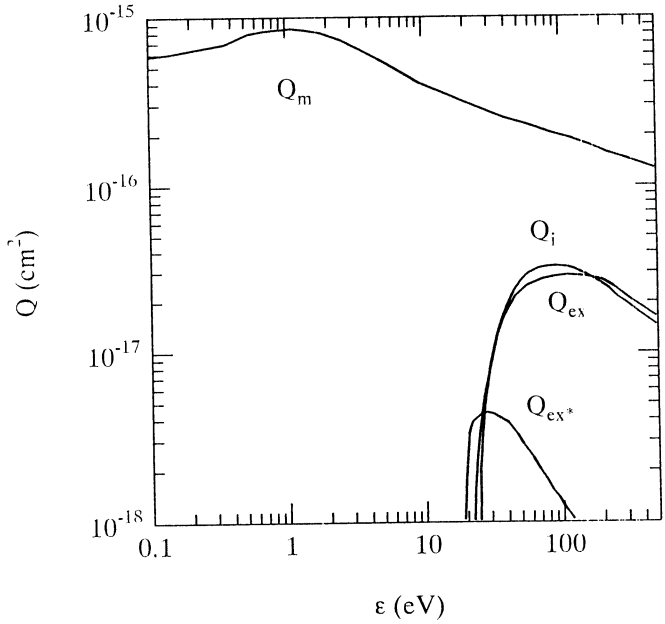

Fig. 1. Cross sections for He where Q_m is the momentum transfer cross section, Q_{ex*} the excitation cross section to the metastable state, Q_{ex} a grouped cross section to excitation states except the metastable state, and Q_i the ionisation cross section.

3. Procedure for the Coefficient Analysis

The α, η and secondary ionisation coefficient γ_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):

$$J = J_0 \frac{\alpha \exp[(\alpha - \eta)d]/(\alpha - \eta)}{1 - [\alpha\gamma_T/(\alpha - \eta)]\{\exp[(\alpha - \eta)d] - 1\}},$$

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 α and η 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.

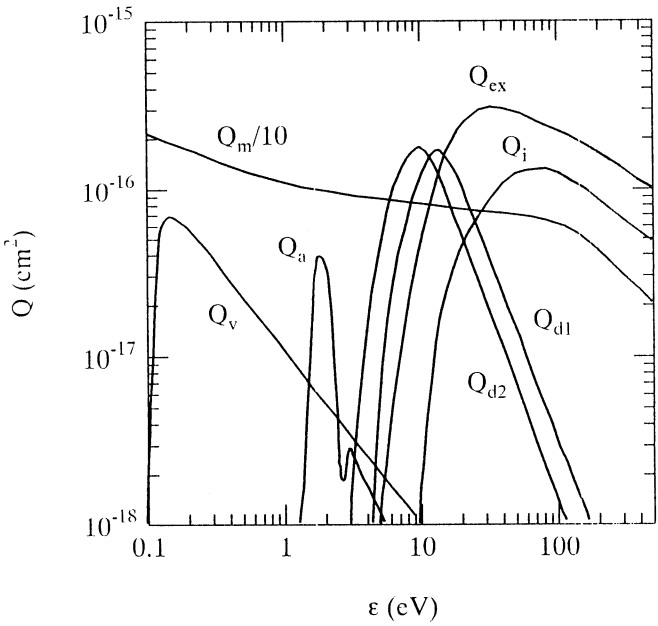

Fig. 2. Cross sections for NO_2 where Q_m is the momentum transfer cross section, Q_v the vibrational excitation cross section, Q_{d1} and Q_{d2} the dissociation cross sections for $NO_2 \rightarrow O+NO$ and $NO_2 \rightarrow N+O_2$ respectively, Q_a the electron attachment cross section, Q_{ex} a 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 α and η was calculated by a Boltsmann 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 α and η 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 6*c*.

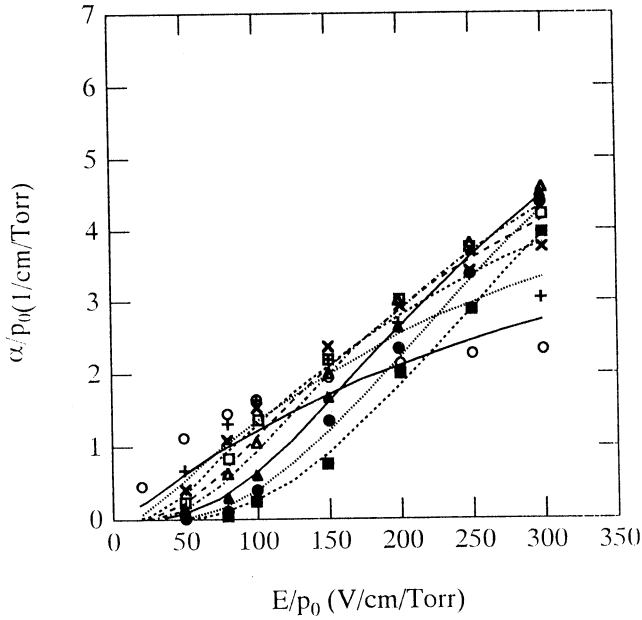

Fig. 3. Coefficient α/p_0 as a function of E/p_0 for experimental values $K = 0$ (He), open circles; 0·1, pluses; 0·2, crosses; 0·3, open squares, 0·4, open triangles; 0·6, closed triangles; 0·8, closed circles; and 1·0 (NO_2), solid squares. The curves are the BE analysed values.

6. Results and Discussion

(6a) Ionisation Coefficient α/p_0

Electron impact ionisation coefficients α/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 α 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, α/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 α/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 α/p_0 value depends significantly on K. In He gas the experimental values of α/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.

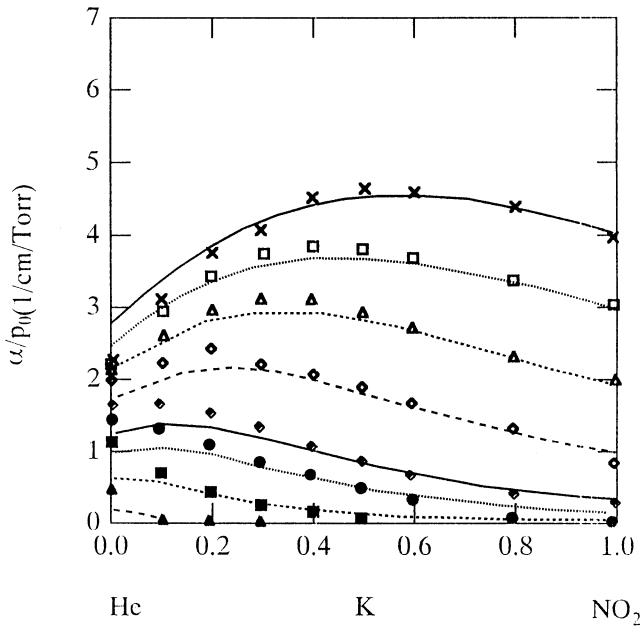

Fig. 4. Coefficient α/p_0 as a function of K for experimental values $E/p_0 = 300\ \mathrm{V\,cm^{-1}\,Torr^{-1}}$, crosses; 250, open squares; 200; open triangles; 150, open diamonds; 100, half-filled diamonds; 80, closed circles; 50, closed squares; and 20, closed triangles. The curves are the BE analysed values.

The coefficient α/p_0 does not change linearly with K as shown in Fig. 4. For $E/p_0 > 100\ \mathrm{V\,cm^{-1}\,Torr^{-1}}$, a maximum appears in the α/p_0 versus K curves. The value of K at which the α/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 $100\ \mathrm{V\,cm^{-1}\,Torr^{-1}}$ for NO_2 (Okumura *et al.* 1994). In the mixtures, not shown in the present figures, this limiting value decreases from $100\ \mathrm{V\,cm^{-1}\,Torr^{-1}}$ with decreasing K.

(6b) Attachment Coefficient η/p_0

The electron attachment coefficient η/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, η/p_0 does not vary with pressure. As seen in Fig. 5, though the experimental values of η/p_0 are scattered, in the E/p_0 range where the η/p_0 values are measured they agree reasonably well with the BE values. It is expected that η/p_0 will increase significantly with decreasing E/p_0 for a low E/p_0 region, based on the BE result.

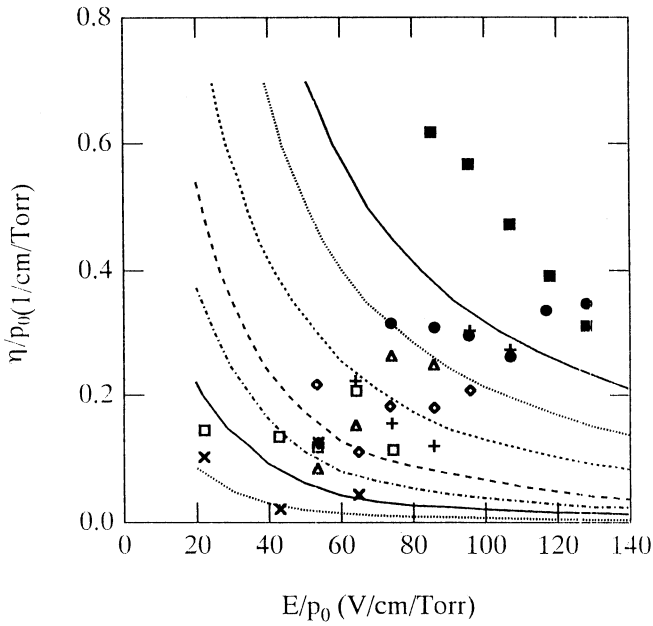

Fig. 5. Coefficient η/p_0 as a function of E/p_0 for experimental values $K = 0{\cdot}2$, crosses; $0{\cdot}3$, open squares; $0{\cdot}4$, open triangles; $0{\cdot}5$, inverted triangles; $0{\cdot}6$, plusses; $0{\cdot}8$, closed circles; and $1{\cdot}0$ (NO_2), solid squares. The curves are the BE analysed values.

(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_2O (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_2O and the total value of the scattering of NO_2.

The molecular weights of NO_2 and N_2O are quite close: 46 for NO_2 and 44 for N_2O. However, there are significant differences in molecular configuration: i.e. NO_2 has a bend shape and N_2O is a linear molecule. The dipole moment of NO_2 is larger than the N_2O value by a factor of $1{\cdot}9$. So, even if it might not be completely correct to use the Q_m of N_2O as a first approximation, the Q_m of N_2O (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 $0{\cdot}16$, $0{\cdot}093$ and $0{\cdot}2$ eV (Laborie *et al.* 1971) and grouped them with a threshold of $0{\cdot}093$ and the maximum of 7×10^{-17} cm^2 at $0{\cdot}15$ eV as shown in Fig. 2. The dissociation cross sections with the threshold energies of $3{\cdot}11$ eV for the reaction $NO_2 \rightarrow O+NO$ (Q_{d1}) and of $4{\cdot}50$ eV for the reaction $NO_2 \rightarrow N+O_2$ (Q_{d2}) (Laborie *et al.* 1971) are shown in Fig. 2.

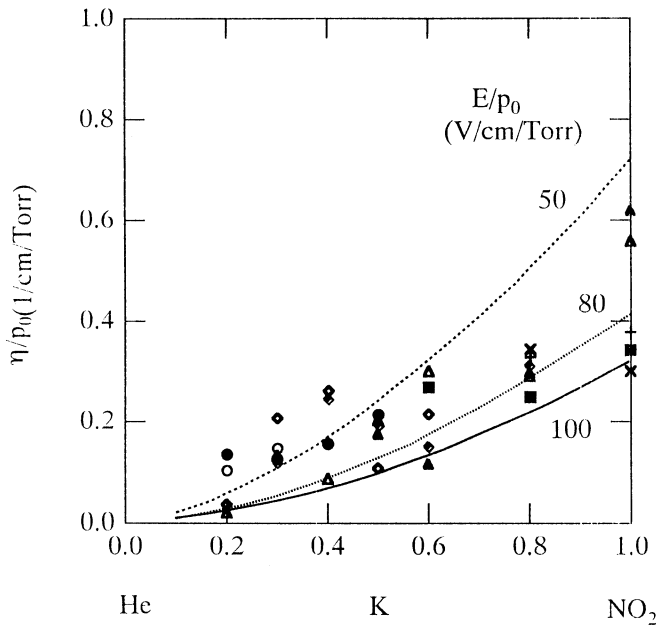

Fig. 6. Coefficient η/p_0 as a function of K for experimental values $E/p_0 = 130\ \mathrm{V\,cm^{-1}\,Torr^{-1}}$, crosses; 110, pluses, 90, open triangles, 80, closed triangles; 70, half-filled diamonds; 60, open diamonds; 50, closed circles; and 30, closed squares. The curves are the BE analysed values.

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 η/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 α and η 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 $1{\cdot}4\times10^{-17}$ cm^2 at 80 eV.

The values of α and η depend strongly on the values of Q_m, Q_i and Q_a. When we varied these three cross sections by 10%, α and η for NO_2 changed by more than 20% and it became difficult to obtain consistent α and η 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 α/p_0 and attachment η/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 α and η, preliminary cross sections for NO_2 have been estimated.

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