

ION-MOLECULE REACTIONS AND ION KINETICS IN DC TOWNSEND DISCHARGES IN DIELECTRIC GASES

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ABSTRACT

The transport of positive and negative ions plays an important role in the initiation and behavior of discharges in gaseous dielectrics. In many cases, the identities, intensities, and kinetic energies of ions are determined by ion-molecule collisions experienced by ions while they are accelerated through the discharge. To help delineate the role of various collisional processes, such as charge-exchange collisions, collisional detachment, and ion conversion, we have measured the kinetic-energy distributions (KEDs) of positive and negative ions formed in dc Townsend discharges generated in O₂ and SF₆ at high electric field-to-gas density ratios (E/N). The relative abundances and mean energies of the ions are obtained from these measurements, and the effective cross sections for the ion-molecule reactions, in some cases, may be calculated. The availability of ion-molecule collision cross sections for the negative ions formed in O₂ and SF₆ enable a reasonable understanding of the KED data. However, attempts to analyze the positive ion KED data for these two gases highlight the lack of fundamental ion-molecule cross section data for positive ions formed in these discharges.

INTRODUCTION

Understanding the details of ion production and transport in electrical discharges is of importance to both the semiconductor industry, which uses gas-phase discharges for microelectronic device production, and the electric equipment industry, which uses electronegative gases as high voltage insulation. Oxygen is a gas of interest in both of these areas because of its common usage in plasma discharges for etching and cleaning processes,

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and because of its nearly universal presence in high voltage insulation systems as an impurity. Sulfur hexafluoride (SF_6) is of interest due to its overwhelming use as a dielectric gas in high voltage equipment, and its use by the semiconductor industry in a wide variety of etching processes.

In this paper, we utilize a dc Townsend discharge to measure the kinetic energy distributions (KEDs) of positive and negative ions striking the grounded electrode for values of E/N ranging from $2 \times 10^{-18} \text{ Vm}^2$ to $40 \times 10^{-18} \text{ Vm}^2$ (2 kTd to 40 kTd). These values of E/N are comparable to those observed in the sheath regions of glow discharges.

Analysis of the identities, energies, and intensities of the ions generated in a discharge enables a qualitative understanding of the ion-production processes, and subsequent ion-molecule collision processes that affect the flux of ions through the discharge. Additionally, the shapes of the energy distributions allow a determination of the range of E/N for which equilibrium conditions exist for the ions. Information determined from this simple dc parallel-plate discharge system is useful in modeling complex discharges, and in guiding the investigation of the significant ion-molecule reactions occurring in other types of electrical discharges.

EXPERIMENT

The apparatus used for these experiments is essentially identical to that used to investigate Townsend discharges in the rare gases.¹ The only significant change is the ability to reverse the polarity of the electrodes, and of the appropriate voltages in the energy analyzer-mass spectrometer, to allow detection of negative ions. Briefly, the discharge cell consists of two parallel, stainless steel plates that are 11 cm in diameter and spaced 2 cm apart. A 100 μm hole in the center of the lower electrode (the cathode when detecting positive ions and the anode when detecting negative ions) allows the sampling of ions by a quadrupole mass spectrometer with an electrostatic ion-energy analyzer. The kinetic energy distribution of the flux of ions striking the grounded electrode is measured by setting the quadrupole mass spectrometer to a specific mass, and then scanning the transmission energy of the ion-energy analyzer. The energy resolution of the energy analyzer is approximately 4 eV (full width at half maximum), and analysis of the transmission characteristics of the ion-energy analyzer indicates that ion energies below 10 eV are not reliable. Above 10 eV, both the ion-energy analyzer and the quadrupole mass spectrometer were tuned such that the ion transmission is independent of the mass and energy of the ion.

OXYGEN RESULTS AND DISCUSSION

Kinetic energy distributions for ions sampled from a Townsend discharge in oxygen were measured for values of E/N ranging from $2 \times 10^{-18} \text{ Vm}^2$ to $40 \times 10^{-18} \text{ Vm}^2$. Figure 1 shows representative measured KEDs for a Townsend discharge in oxygen at $E/N = 15 \times 10^{-18} \text{ Vm}^2$ (15 kTd). As can be seen from the figure, O_2^+ is the dominant ion, followed by the only other ions detected, O^+ , O_2^- , and O^- . This order of intensities was observed for all values of E/N investigated here. For values of E/N less than $15 \times 10^{-18} \text{ Vm}^2$ the measured KEDs exhibit a Maxwellian shape that is reflected by the linear slope of the distribution when plotted on a semi-logarithmic graph (see line in Fig. 1a). This behavior is indicative of ions (*i*) whose motion takes place in a uniform electric field, (*ii*) whose primary collision process is symmetric charge exchange, and (*iii*) for whom equilibrium conditions apply (i.e., the ions have experienced many collisions).² The KEDs for O_2^+ exhibit increasing deviations from this Maxwellian behavior as the E/N increases above $15 \times 10^{-18} \text{ Vm}^2$. This is just barely evident

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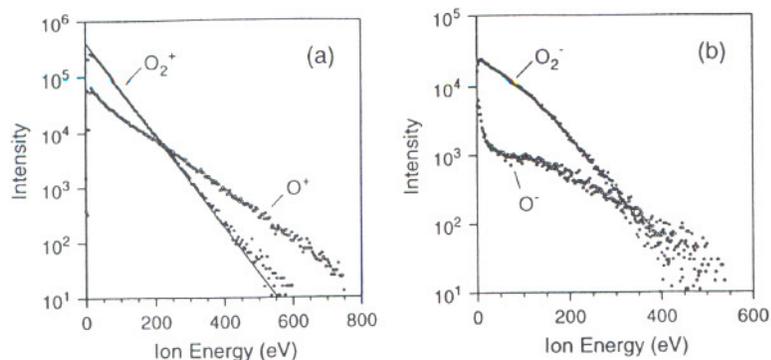


Fig. 1. Kinetic energy distributions of ions sampled from an oxygen Townsend discharge with $E/N = 15 \times 10^{-18} \text{ Vm}^2$ (15 kTd).

in the O_2^+ KED shown in Fig. 1a, by the slight deviation at higher energies of the measured data from the linear fit. These deviations indicate the advent of additional energy-loss collision processes (other than symmetric charge transfer), or of the development of non-equilibrium conditions for the O_2^+ ions within the discharge.

The KEDs for O^+ ions exhibit higher mean energies than the KEDs for O_2^+ , often with the maximum ion energy corresponding to the voltage across the discharge gap. This condition is illustrated in Fig. 1a where the maximum ion energy for O^+ equals 750 eV, corresponding to the discharge voltage of approximately 750 V, and is an indication of non-equilibrium conditions for the O^+ ions. The higher mean energies for O^+ ions are due to the fact that the cross section for asymmetric charge exchange is significantly less than for the symmetric process,³ which does not exist for O^+ under these discharge conditions. These conditions are reflected in the observed non-Maxwellian shape of the KEDs for O^+ at all E/N .

The KEDs for O_2^- are determined primarily by symmetric charge-exchange collisions,⁴ and by collisional detachment collisions⁵ that destroy the ion. Below $5 \times 10^{-18} \text{ Vm}^2$, the KEDs for O_2^- are Maxwellian in shape, indicating that symmetric charge exchange is the dominant collisional reaction experienced by the ion. At higher values of E/N , the effect of collisional detachment interactions increases due to the increasing cross section for this process with increasing ion energy.⁵ The effect of collisional detachment is reflected in the KED for O_2^- shown in Fig. 1b by the drop-off in ion intensity at higher energies. The KEDs for O^- are highly non-Maxwellian at all E/N , indicating a complex dependence on several competing, energy-dependent collisional processes, including asymmetric charge exchange⁶ and collisional detachment.⁵

The mean energies of the ions at each E/N may be calculated from the measured KEDs, and are observed to increase with increasing E/N for all ions. For O_2^+ and O_2^- , whose transport is primarily determined by symmetric charge-exchange interactions at low E/N , an effective charge-exchange cross section may be determined from the mean energies.² This effective cross section agrees well with beam-determined measurements of the charge-exchange cross sections for values of E/N below $15 \times 10^{-18} \text{ Vm}^2$ for O_2^+ and $5 \times 10^{-18} \text{ Vm}^2$ for O_2^- .⁷

SULFUR HEXAFLUORIDE RESULTS AND DISCUSSION

The investigation of ion transport in discharges in SF_6 is complicated by the increased number of ions generated in the discharge. Fig. 2 shows a comparison of a standard 70-eV electron-impact mass spectrum⁸ for SF_6 , and a mass spectrum of ions sampled from a

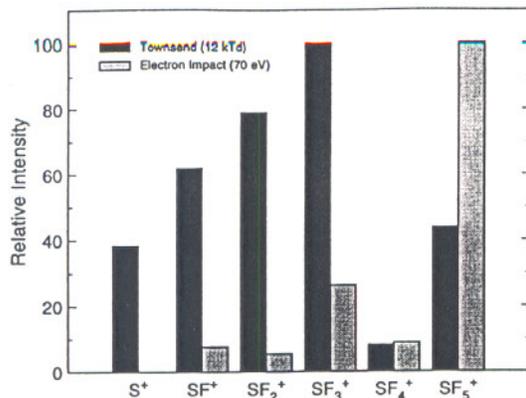


Fig. 2. Mass spectra of positive ions sampled from a Townsend discharge ($E/N \approx 12 \times 10^{-18} \text{ Vm}^2$) in SF_6 , compared with a standard 70-eV electron-impact mass spectrum for SF_6 .⁷

Townsend discharge in SF_6 with $E/N \approx 12 \times 10^{-18} \text{ Vm}^2$. In contrast to the electron-impact spectrum, the lower mass ions dominate the spectrum from the Townsend discharge, a clear indication of the role of ion-molecule reactions in determining the identity of the ions striking surfaces exposed to electrical discharges. The decreased SF_5^+ intensity and increased SF_3^+ intensity observed in the Townsend discharge, relative to the electron-impact mass spectrum, may be attributed to the previously investigated⁸ ion-conversion process



Other ion-conversion processes are responsible for the production of the SF_2^+ , SF^+ and S^+ ions, but little is known about these processes.

Figure 3 shows representative KEDs for the positive ions detected from the SF_6 Townsend discharges at $12 \times 10^{-18} \text{ Vm}^2$. The KEDs exhibit non-Maxwellian shapes for all the ions at all values of E/N investigated here (8 to 20 kTd), reflecting the impact of the complex ion-conversion processes taking place in the discharge. Interestingly, the mean energies of the ions are observed to increase with decreasing mass.

Negative ions in SF_6 are initially formed by electron attachment processes¹⁰ that result primarily in the formation of SF_6^- and SF_5^- . However, the mass spectrum of the negative ions detected from an SF_6 Townsend discharge ($E/N \approx 12 \times 10^{-18} \text{ Vm}^2$), shown in Fig. 4, indicates that F^- is the dominant ion striking the electrode. Since the yield of F^- due to electron attachment processes is significantly lower than for SF_6^- production,¹⁰ this large F^- signal is attributed to the ion-molecule reactions,



that have been shown to possess large cross sections.¹¹

Figure 5 shows KEDs for the four negative ions detected in the SF_6 discharge. SF_6^- and SF_5^- exhibit significantly lower mean kinetic energies than the positive ions, due to reactions (2) and (3), large charge-exchange cross sections, and the manifestation of collisional detachment processes at higher energies.¹¹ In fact the maximum ion energies detected here for

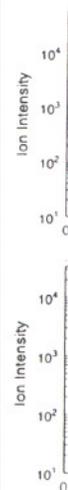


Fig. 3. Townsend

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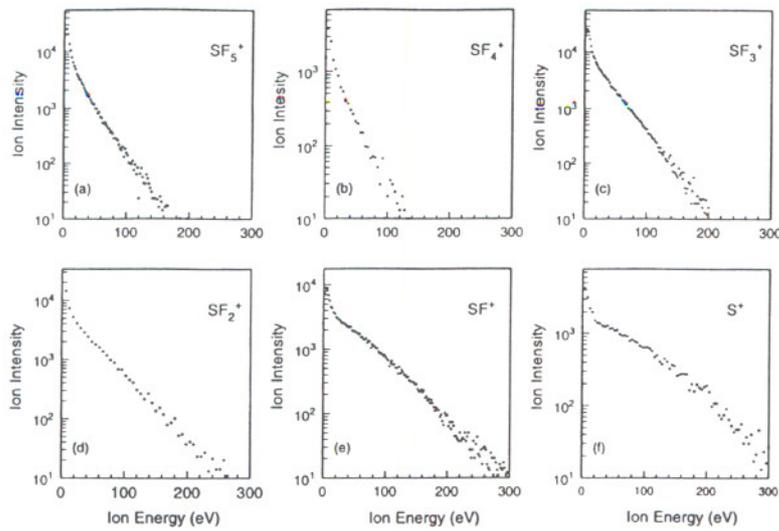


Fig. 3. Kinetic energy distributions for positive ions sampled from an SF₆ Townsend discharge with $E/N = 12 \times 10^{-18} \text{ Vm}^2$.

SF₆⁻ and SF₅⁻ ions nearly correspond with the 90-eV threshold for collisional detachment from SF₆⁻ and SF₅⁻. F₂⁻ is also thought to be formed predominantly by collisional ion conversion of SF₆⁻ and SF₅⁻ ions, however, the ion-molecule collisions between F₂⁻ and SF₆ are unknown.

CONCLUSION

We have measured the mass and energies of the ions striking the grounded electrode in a dc Townsend discharge in pure oxygen and pure sulfur hexafluoride over a wide range of high E/N . For oxygen, O₂⁺ is the dominant positive ion, while O₂⁻ is the dominant negative ion. Analysis of the ion kinetic energy distributions indicate that symmetric charge transfer is the dominant ion-molecule reaction for both ions, although the effects of collisional detachment

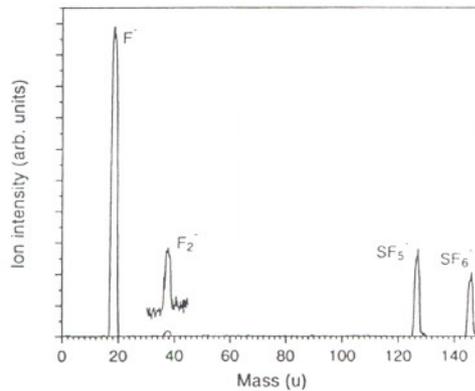


Fig. 4. Mass spectrum of negative ions sampled from an SF₆ Townsend discharge with $E/N = 12 \times 10^{-18} \text{ Vm}^2$.

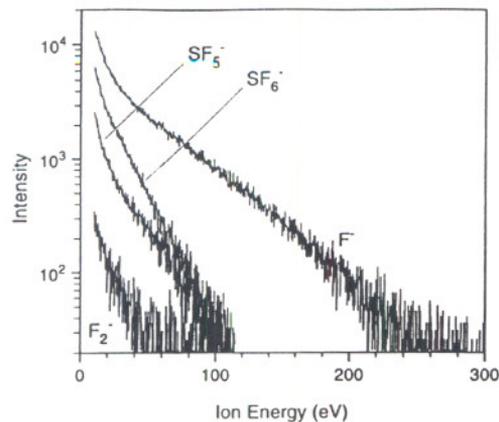


Fig. 5. Kinetic energy distributions of negative ions sampled from an SF₆ Townsend discharge with $E/N \approx 12 \times 10^{-18} \text{ Vm}^2$. The ion signal below 10 eV is not shown (see Experiment section).

are evident in the measured KEDs for O₂⁻ for $E/N > 5 \times 10^{-18} \text{ Vm}^2$. Smaller, but significant, quantities of O⁺ and O⁻ were detected with complex KEDs that are the results of multiple ion-collision processes.

Six positive ions are detected from Townsend discharges generated in SF₆. SF₃⁺ is the dominant ion at all E/N , and is thought to be formed predominantly by an ion-collision process that converts SF₅⁺ to SF₃⁺. The processes responsible for the production of S⁺, SF⁺, and SF₂⁺ are not fully understood. The dominant negative ion is F⁻ which is produced by ion-conversion processes involving collisions of SF₆⁻ and SF₅⁻ with SF₆. The measured KEDs for all of the ions detected in the SF₆ discharge exhibited non-Maxwellian shapes, again resulting from the effects of multiple ion-collision processes.

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DISCUSSION

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DISCUSSION

K. BECKER: Is it possible to attribute the high F^- yield in the SF_6 Townsend discharge to dissociative attachment to SF_x free radicals produced by neutral dissociation of SF_6 ?

M. V. V. S. RAO: It is unlikely. It should be noted that F^- production by dissociative electron attachment to SF_6 is orders of magnitude lower than SF_6^- formation. Even if F^- production from SF_x radicals exists, the rate should be as small as for F^- from SF_6 . Therefore, the enhancement of F^- intensity in our experiment is mainly from $SF_5^- + SF_6 \rightarrow F^- + \text{products}$ and $SF_6^- + SF_6 \rightarrow F^- + \text{products}$, and it is consistent with earlier beam-beam experiments by R. L. Champion and collaborators [J. Chem. Phys. **91**, 2254 (1989)].

W. BOECK: The ion-molecule reactions are important for the extremely low pressure used in your experiments. They have low influence on the process of ionization in the case of usual pressure of 0.1 MPa since the ion energy is much smaller. What is your opinion in this respect?

M. V. V. S. RAO: Obviously the E/N will be lower in discharges at such a high pressure, so the energy distribution of the ions will be completely different than those shown here. However, the ion-molecule reactions discussed here are important for discharges at nearly all pressures.

YICHENG WANG: I have a question about negative ions in O_2 discharges. As you said, negative ions in O_2 discharges are mainly formed via dissociative electron attachment producing O^- . Indeed, it has been observed that O^- ions are dominant in RF O_2 discharges. Yet, your results (Fig.1) show that O_2^- is dominant. Could you say a few words about possible reasons?

M. V. V. S. RAO: The primary process of O^- production in O_2 discharge is by dissociative electron attachment. The production of O_2^- is by the asymmetric charge transfer reaction $O + O_2 \rightarrow O + O_2^-$ which has a large cross section compared to the detachment cross section for O^- . There is also a possibility of O_2^- formed at the electrode surface by ion and/or neutral bombardment during the discharge.

A. GARSCADDEN: Could you please define the discharge instability that you alluded to? Is it temporal or spatial, current runaway or oscillation? The point is that there is information in the oscillation limits on the saturation of attachment and ionization.

M. V. V. S. RAO: It is oscillation. We did not investigate it as it was not the point of the present experiment.