Negative Ion-Neutral Reactions in Townsend Discharges

J. K. Olthoff[1] and M. V. V. S. Rao[2]

National Institute of Standards and Technology
Gaithersburg, Maryland, USA 20899-8113

Abstract – Relative intensities and translational ion-flux energy distributions are presented for negative ions sampled from Townsend discharges in O_2, SF_6, and CF_4 for a high range of density reduced electric fields greater than 2×10^{-18} V m^2 (> 2 kTd). These results are discussed in light of relevant ion-molecule reactions where available.

1. Introduction

Understanding the transport of negative ions is an important aspect of understanding electrical discharges in electronegative gases, particularly those used as gaseous dielectrics. In this paper we review some recent work performed in our laboratory in which we measured the energies and relative intensities of negative ions produced in dc Townsend discharges. These discharges emulate the high field conditions found in many discharge sheaths, yet they are relatively simple in that the ions are usually being accelerated under swarm conditions.

In cases where ion-molecule cross sections are available many of the characteristics of the measured ion flux energy distributions and the relative ion intensities may be qualitatively explained. In cases where few cross sections are available, the ion-energy data often suggest the significant reactions affecting the transport of the ions.

2. Experiment

The experimental apparatus used to obtain the data presented here has been described previously in our papers presenting results obtained for Townsend discharges in rare gases [1] and in oxygen [2]. Briefly, the discharge cell consists of two flat, parallel, 11-cm-diameter stainless steel electrodes separated by a 2 cm gap and surrounded by a cylindrical quartz tube. The discharge is generated by introducing a gas between the plates, and then biasing the upper electrode either positively or negatively in order to sample positive or negative ions, respectively, at the grounded electrode. Ions from the discharge pass through a 0.1-mm sampling orifice in the grounded electrode and enter a differentially pumped, 45° electrostatic ion-energy analyzer and quadrupole mass spectrometer system. The resolution of the mass spectrometer was approximately 1 u (amu), and the resolution of the electrostatic energy analyzer was maintained at 4 eV, independent of the mass and energy of the ion. The energy distributions of ions striking the grounded electrode are measured by setting the quadrupole to transmit ions of a particular mass, and then scanning the potential of the energy analyzer. The resulting distribution function is an ion-flux energy distribution, i.e., the number of ions per second with energy between ε and $\varepsilon + d\varepsilon$ that strike a particular area of the grounded electrode [1-3].

In a Townsend discharge the currents are sufficiently low (<100 μA) such that space charge effects are negligible, i.e. space charge does not significantly affect the applied electric field

[1]Electronic address: james.olthoff@nist.gov

[2]Present Address: MS 229-1, NASA/Ames Research Center, Moffet Field, CA 94035

between the electrodes. Thus assuming the ions experience many collisions as they travel across the gap, the energies of the ions will be dependent only upon the ratio of the electric field strength to the gas number density, *E/N*. The electric field strength, *E*, in the discharge gap is assumed to be given by V_d/d, where *d* is the interelectrode gap spacing (2 cm) and V_d is the voltage drop across the gap. The gas density *N* is determined from the gas pressure in the gap region as measured by a capacitive manometer (baratron), and is usually between 5 Pa and 50 Pa.

3. Results and Discussion

3.1. Oxygen

Two negative ions, O_2^- and O^- were detected from Townsend discharges in oxygen. Typical ion-flux energy distributions are shown in Fig. 1 for both ions at an *E/N* value of approximately 15×10^{-18} V m^2 (15 kTd). The measured intensity of O_2^- exceeded that of O^- at all *E/N* studied for O_2 (2×10^{-18} V m^2 to 30×10^{-18} V m^2), but nearly equal intensities were observed at the lowest *E/N*. In this range of high *E/N*, O^- is the only ion generated by direct interactions with electrons (i.e., dissociative attachment [4] or polar dissociation [5]), so the large flux of O_2^- ions must be attributed to gas phase ion-molecule reactions, such as asymmetric charge transfer involving O^-, or to O_2^- production processes at the electrode surfaces [6].

At low *E/N* the ion-flux energy distributions of O_2^- are nearly Maxwellian which is indicative of a single ion-molecule collision dominating the transport of the ion across the gap. For O_2^- symmetric charge exchange has been shown to be the dominant collision process affecting the ion energy [2]. At higher *E/N* the shape of the energy distribution exhibits a reduction in intensity at the higher energies that is attributable to the destruction of O_2^- ions by collisional electron detachment. The effect of collisional detachment is also evident in the fact that the maximum energies of both the O_2^- and O^- ions are significantly lower than observed for their positive ion counterparts [2].

The ion-flux energy distributions for O^- exhibit complex shapes at all *E/N* similar to that shown in Fig. 1. While the energies of O^- ions would clearly be affected by asymmetric charge exchange and collisional detachment reactions, the complex ion-flux energy distributions are not fully understood and suggest the need for additional cross section measurements and modeling.

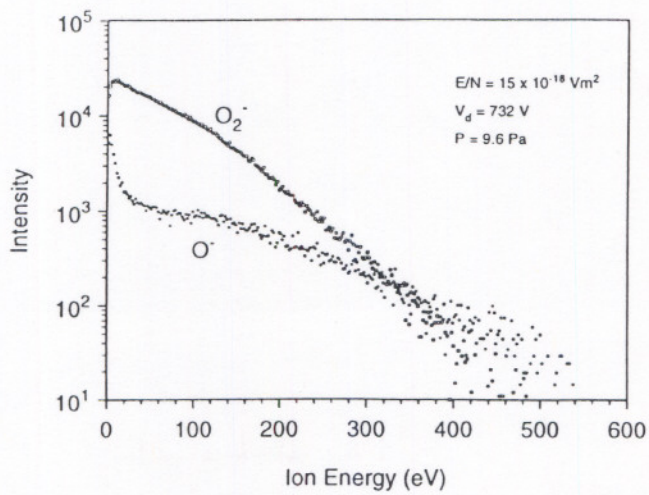

FIG. 1. Ion-flux energy distributions for negative ions sampled from a Townsend discharge in oxygen.

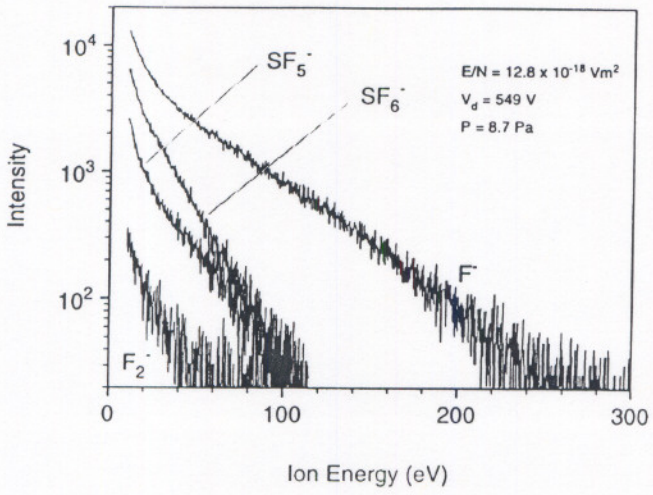

FIG. 2. Ion flux energy distributions for negative ions sampled from a Townsend discharge in sulfur hexafluoride.

3.2. *Sulfur Hexafluoride*

The composition of the ion flux for SF_6 discharges is more complex than for O_2. Four negative ions, SF_6^-, SF_5^-, F_2^-, and F^-, were detected from Townsend discharges generated in SF_6. Typical ion-flux energy distributions for these ions are shown in Fig. 2 for a value of $E/N = 12.8 \times 10^{-18}$ V m^2. It is clear from the figure that F^- was the dominant ion observed, with SF_6^-, SF_5^-, and F_2^- exhibiting subsequently less intensities. This relative order of intensities was observed for nearly all values of *E/N* studied here (5.5×10^{-18} V m^2 to 18×10^{-18} V m^2), except at 5.5×10^{-18} V m^2 where the intensity of SF_5^- slightly exceeded that of SF_6^-.

The kinetic energy distributions of SF_6^- and SF_5^- exhibit Maxwellian shapes at lower *E/N* values, but begin to deviate from this shape with increasing *E/N*. This suggests an increasing number of ion production and/or conversion processes affecting the ion transport as the value of *E/N* increases. The energy distributions for F^- are non-Maxwellian at all values of E/N investigated here.

The following ion-conversion reactions can explain much of the observed behavior of the negative ions in the discharges:

$$SF_6^- + SF_6 \rightarrow F^- + SF_5 + SF_6 \quad (1)$$
$$SF_5^- + SF_6 \rightarrow F^- + SF_4 + SF_6 \quad (2)$$
$$SF_6^- + SF_6 \rightarrow F + SF_5^- + SF_6 \quad (3)$$
$$SF_6^- + SF_6 \rightarrow SF_6 + SF_6^- \quad (4)$$
$$SF_5^- + SF_6 \rightarrow SF_5 + SF_6^- \quad (5)$$
$$F^- + SF_6 \rightarrow F + SF_6^- \quad (6)$$
$$SF_5^- + SF_6 \rightarrow F_2^- + \text{products} \quad (7)$$
$$SF_6^- + SF_6 \rightarrow F_2^- + \text{products} \quad (8)$$

Measurements of electron attachment cross sections indicate that SF_6^- and SF_5^- are the dominant ions produced by direct electron interactions with SF_6 [7]. Thus, the abundance of F^- in the Townsend discharge must be attributed to Reactions 1 and 2 which efficiently convert SF_6^- and SF_5^- to F^-. Previous measurements [8] have shown that the magnitudes of cross sections for Reactions 1 and 2 increase with increasing collision energy to approximately 35 Å^2, and are significantly larger than the cross sections for the other reactions listed above. Additionally,

Reaction 3, which converts SF_6^- to SF_5^-, exhibits a significant cross section at low energies which is consistent the nearly equal intensities of SF_6^- and SF_5^- ions, particularly at low *E/N*.

The charge transfer reactions 4 and 5 also affect the energy distributions of SF_6^- and SF_5^-, contributing to their lower mean energies observed in the Townsend discharges compared to F^-. The charge exchange reaction 6 which destroys F^- is relatively small compared to those for SF_6^- and SF_5^- which explains the larger energies of the F^- ions.

Little is known about the production processes for F_2^- (Reactions 7 and 8), or about potential ion-molecule collisions involving F_2^-. However, due to the low intensity of the ion and the low observed ion energies, one expects that the cross sections for production are small, and the cross sections for ion-molecule reactions involving F_2^- may be large.

Collisional detachment reactions have no obvious effect upon the measured ion-flux energy distributions, due to their relatively small cross sections and, for SF_6^- and SF_5^-, their very high thresholds [8]. However, it is interesting to note that the mean energies of the negative ions are in all cases observed to be lower than their positive ion counterparts for the same discharges.

3.3. Carbon Tetrachloride

For CF_4, only F^- exhibited sufficient signal intensity to allow the measurement of ion flux energy distributions, although a small amount of CF_3^- was detected. The measured distributions for F^- exhibited complex shapes, similar to those observed for O^- (Fig. 1). No cross sections are available for negative ions in CF_4, except for collisional electron detachment of F^- [9]. The magnitude of that cross section is significant (exceeding 15 $Å^2$ at 50 eV), which in conjunction with the low electron attachment cross sections [10], is consistent with the low observed intensities of negative ions in CF_4.

4. Conclusions

An investigation of the energies and intensities of negative ion fluxes from Townsend discharges aids in establishing a simple understanding of the physics and chemistry of ion transport. These discharges are significantly simpler than many other discharges, such as low temperature radio frequency discharges, and may lend themselves to various modeling efforts. The use of available ion-molecule cross sections enables a qualitative understanding of many of the observed characteristics of the ion transport. In some cases the measured ion-energy data allows conclusions to be drawn about cross sections for which no data are available.

5. References

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