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INFLUENCE OF WATER VAPOR AND DECOMPOSITION PRODUCTS ON THE POSITIVE- AND NEGATIVE-ION SPECTRA OF SF_6 CORONA

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Abstract

We report on the positive- and negative-ion spectra obtained from in-situ mass spectrometric analyses of ions sampled from corona disharges in SF_6 at P = 6.7 kPa (50 Torr). In positive-ion spectra the presence of water vapor results in the formation of water cluster ions of the form $H^+(H_2O)_n$. The distribution of cluster sizes shifts to smaller clusters as the water vapor content decreases. In addition to the SF_6 fragment ions (SF_5^+, SF_3^+, and SF_2^+), which are observed under relatively dry conditions, the hydrated species $SF_5^+(H_2O)$ is observed down to water additions of only 40 ppm, the lowest concentration studied. In addition, the ion detected at mass 197 is believed to be the complex $SF_3^+(SF_4)$ where SF_4 is an important neutral by-product of SF_6 discharges. In negative-ion spectra, the influence of water vapor is manifested indirectly by the formation of HF clusters of the form $F^-(HF)_n$. HF is believed to be formed by reaction of F, which is produced from the fragmentation, $SF_6 \rightarrow SF_5 + F$, with H_2O to form HF + OH. As the water vapor content is reduced, the size of $F^-(HF)_n$ clusters is reduced as well. Other clustered species observed include $OH^-(H_2O)_n$ and $OH^-(HF)_n$. The role of other decomposition by-products, such as SOF_4 and SO_2, of SF_6 corona on the positive- and negative-ion spectra will also be discussed.

Introduction

Corona discharges in SF_6 result in the formation of charge carriers the nature of which depend on impurities such as water and HF and on decomposition by-products produced by the corona discharge. Any complete model of SF_6 corona discharges at high pressures will require identification of the positive- and negative-charge carriers. By obtaining mass spectra at pressures low enough (50 Torr) to observe ions representative of the species emerging from the discharge and by adding water and other contaminants, we hope to provide information on reaction pathways useful toward understanding the formation of ions produced at higher pressures approaching atmospheric pressure and above.

In prior work on the negative ion chemistry in SF_6 corona, we have observed the influence of the products of SF_6 corona, such as SOF_4, SiF_4 (when glass or ceramic is present), SO_2, and HF, on the fate of SF_6^- [1]. Reactions of the form

$$SF_6^- + X \rightarrow XF^- + SF_5 , \qquad (1)$$

where X = SOF_4, SiF_4, SO_2, and HF, have rate constants $k_x \gtrsim 10^{-10}$ cm^3/s [2]. In addition, clustering reactions involving HF were also observed, leading to $F^-(HF)_n$, $SF_6^-(HF)$, $SOF_5^-(HF)$ as well as other negative ions clustered to HF. We report here on the influence of water vapor added to dry SF_6 on both the positive- and negative-ion spectra.

Experiment

The corona discharge was produced in a point-to-plane geometry in a discharge chamber attached to a differentially pumped quadrupole mass spectrometer. The point electrode was made of Pt/Ir with a tip radius less than 10^{-6} m. Either positive or negative high voltage was applied to the needle while the plane electrode housing the 3×10^{-6} m diameter sampling aperture was held at ground potential. Positive ions were sampled from positive polarity discharges, and negative ions were sampled from negative polarity discharges. Ions exiting the sampling aperture were directed into a quadrupole mass filter having a mass range of 3-1000 amu. For this work mass spectral data are presented in the range 10-210 amu where unit mass resolution was maintained.

The Pt/Ir needle was mounted to a linear motion feed-through which permitted external control of the point-to-plane gap. For the data reported here, the gap was set to 2 mm, and the corona current was set to 0.5×10^{-6} A for both positive and negative corona discharges. The SF_6 gas pressure was maintained at 6.7 kPa (50 Torr) as measured by a capacitance manometer with a 0-1000 Torr range. At P = 6.7 kPa the corona voltages employed were +1450 and -850 V, respectively, for

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positive and negative polarity corona. While the negative polarity high voltage was unaffected by the addition of water vapor for water concentrations in the range 0–600 ppm, the positive polarity high voltage had to be adjusted so as to maintain constant current (0.5×10^{-6} A) upon addition of water vapor. The added water vapor content was measured by another capacitance manometer with ~0–10 Torr range with resolution of 10^{-3} Torr.

In Fig. 1 is plotted the log of the applied voltage as a function of the log of the partial pressure of H_2O, showing a monotonic decrease with increasing H_2O. The presence of moisture has also been found by Van Brunt [3] to influence the size and pulse rate of corona pulses for positive polarity corona qualitatively consistent with the effect of moisture on the V-i characteristics observed here.

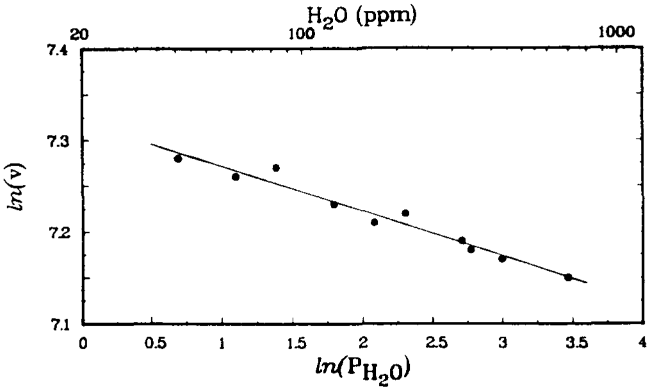

Fig. 1. Log-log plot of applied voltage as a function of water partial pressure in 50 Torr SF_6 for positive corona at constant current, $i_c = 0.5 \times 10^{-6}$ A.

<u>Results and Discussion</u>

"Dry" SF_6. In Fig. 2 a,b are shown the positive and negative ion spectra taken at $i_c = 0.5 \times 10^{-6}$ A. Also shown in the figure (2c) is the positive ion 70-eV electron-impact mass spectrum of SF_6. The positive ion corona spectrum is similar to the electron impact spectrum in that SF_6^+ is the major ion and the lower fragments SF_3^+ and SF_2^+ are formed. The relatively intense SF_2^+ ion observed in the positive corona spectrum is notable since considerable electron energy is required for the formation of this ion by

$$e + SF_6 \rightarrow SF_2^+ + (4F) + 2e \qquad (2)$$

assuming that it is formed in a single collision, which is probably the case since the spectrum does not depend strongly on the corona current. In Table 1 are listed the threshold energies [4] for electron impact fragmentation of SF_6. To produce the SF_2^+ fragments, electron energies in excess of 26.8 eV are required. The SF^+ ion fragment, albeit weak and not shown in the figure, has also been observed under dry conditions. Extensive fragmentation of SF_6 by corona has also been observed by Sigmond [5] at lower pressures ($p < 2$ Torr). The absence of SF_4^+ in the positive corona spectrum suggests that it is removed by reaction in the discharge. Reactions occurring outside the discharge with SF_6 contaminants would be expected to form additional ions. It is believed that SF_4^+ is formed initially, since apparently there is sufficient electron energy in the discharge to form the lower fragments SF_3^+ and SF_2^+. A fast reaction such as the ion-ion recombination process

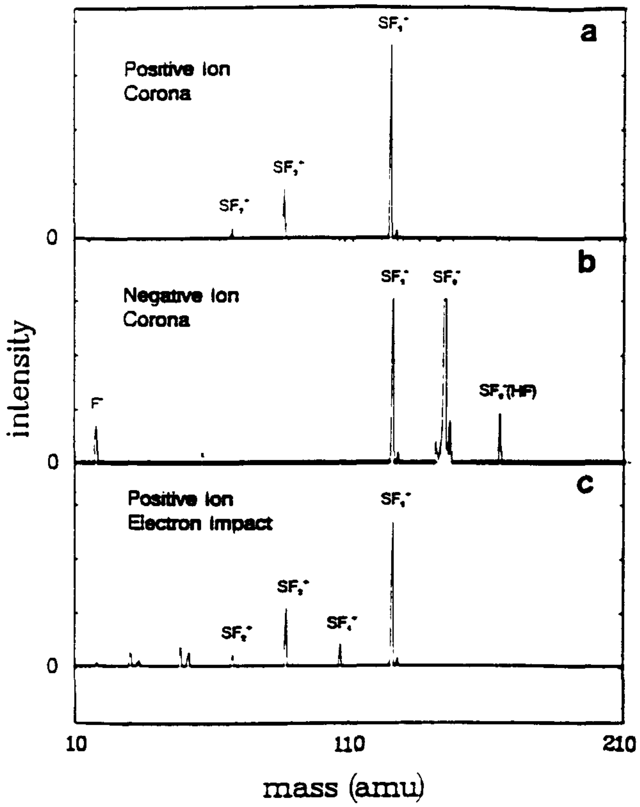

Fig. 2. Mass spectra in the mass range 10–210 amu for (a) Positive corona-positive ions, (b) Negative corona-negative ions, and (c) Positive ion-electron impact for SF_6 without water addition.

Table 1. Threshold energies for positive ion fragments produced by electron inpact on SF_6*

Ion	Threshold Energy (eV)	Ion	Threshold Energy (eV)
SF_5^+	15.9	S^+	37.3
SF_4^+	18.9	F^+	35.8 ± 1.0
SF_3^+	20.1	SF_4^{++}	40.6 ± 0.5
SF_2^+	26.8 ± 0.3	SF_3^{++}	
SF^+	31.3̄ ± 0.3	SF_2^{++}	46.5 ± 0.5

*Dibeler and Mohler, J. Res. Natl. Bur. Stand. 40, 25 (1948).

$$SF_4^+ + SF_6^- \rightarrow SF_5 + SF_5 \qquad (3)$$

may be responsible for the disappearance of this ion. Also observed (but not shown in the figure) is the positive ion at m/e = 197. This ion is believed to be the complex $SF_3^+(SF_4)$ based on its m/e and on measurements of the ratio of the isotope at m/e = 199 amu to the isotope at 197 amu, indicating that it is probably a disulfur ion.

The negative ion spectrum is shown in Fig. 2b. The major ions are SF_6^- and SF_5^-. Also observed are peaks at m/e = 19, 39, 59, 143, an 166 amu, identified as F^-, $F^-(HF)$, $F^-(HF)_2$, SOF_5^-, and $SF_6^-(HF)$. The SOF_5^- is formed by F^- exchange [6,7]

$$SF_6^- + SOF_4 \rightarrow SOF_5^- + SF_5 \qquad (4)$$

where SOF_4 is a neutral by-product of SF_6 corona and a possible contaminant in SF_6. The HF is also believed to be a contaminant in the SF_6 gas. Since SOF_4 is a neutral by-product of SF_6 corona, reaction 4 is an important process for the removal of SOF_4 and, consequently, reduction of SF_6^- as a major negative charge carrier [2].

Effect of H_2O on Positive Ions. At small water addition (40 ppm at 50 Torr SF_6), the first observable change in positive corona spectrum is the appearance of the ion at m/e = 145, identified as the cluster $SF_5^+(H_2O)$. As water is increased, the $SF_5^+(H_2O)$ ion intensity increases relative to SF_5^+. A plot (Fig. 3) of the intensity ratio I_{145}/I_{127} as a function of the water content shows a monotonic increase. The other SF_6 fragment ions SF_3^+ and SF_2^+ are relatively unaffected by water addition in the range 0-600 ppm H_2O. In Fig. 4 we show the ion intensities of SF_5^+, SF_3^+, SF_2^+, $SF_5^+(H_2O)$, and SOF_3^+ as a function of water content. The SF_5^+ ion intensity drops steadily with increasing water content, while SF_3^+ and SF_2^+ exhibit only a slight decline in the 15-32 mTorr range of H_2O partial pressures. The $SF_5^+(H_2O)$ cluster, on the other hand, increases to a maximum at $P_{H_2O} \sim 10$ mTorr, then decreases with increasing water content. However, SOF_3^+ increases with increasing water content throughout the range of H_2O content studied. This may be due to the reaction

$$SF_5^+ + H_2O \rightarrow SOF_3^+ + 2HF \quad . \qquad (5)$$

Such a reaction must compete with the clustering reaction

$$SF_5^+ + H_2O + M \rightarrow SF_5^+(H_2O) + M \ . \qquad (6)$$

where $M = SF_6$ is a third body needed to stabilize the cluster.

A third process, charge exchange,

$$SF_5^+ + H_2O \rightarrow H_2O^+ + SF_5 \qquad (7)$$

can lead to the formation of water cluster ions, $H^+(H_2O)_n$, n = number of H_2O molecules in the cluster.

Water clusters such as these are known to form [7] according to the reaction

$$H^+(H_2O)_n + H_2O + M \rightleftarrows H^+(H_2O)_{n+1} + M \ . (8)$$

where $M = SF_6$ in these studies. The reverse reaction, after sufficient time, can result in the establishment of a distribution of cluster sizes, based on the concentration of water. Figure 5 shows a typical positive corona spectrum with relatively high water content (300 ppm H_2O/SF_6). The $H^+(H_2O)_n$, n = 1-4, cluster series is noted in the figure. The distribution of ions shift to higher n with increasing water content.

Other water clustered ions which we observed include $SF_3^+(H_2O)_n$, n = 0-,2; $SOF_3^+(H_2O)$; and the ion observed at m/e = 165 which is believed to be the cluster $SF_5^+(H_2O)(HF)$.

Effect of H_2O on Negative Ions. For water additions of as little as 100 ppm, ion peaks at 39 and 59 amu increase in intensity substantially. These are most likely the cluster ions $F^-(HF)$ and

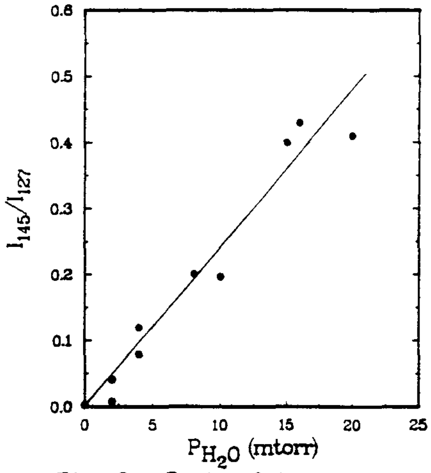

Fig. 3. Ratio of ion intensity at mass 145 [$SF_5^+(H_2O)$] to mass 127 (SF_5^+) as a function of water partial pressure.

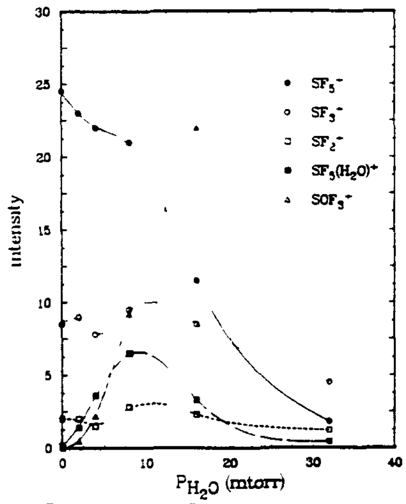

Fig. 4. Positive ion intensity as a function of H_2O partial pressure in 50-Torr SF_6 positive corona for the ions SF_5^+, SF_3^+, SF_2^+, $SF_5^+(H_2O)$ and SOF_3^+.

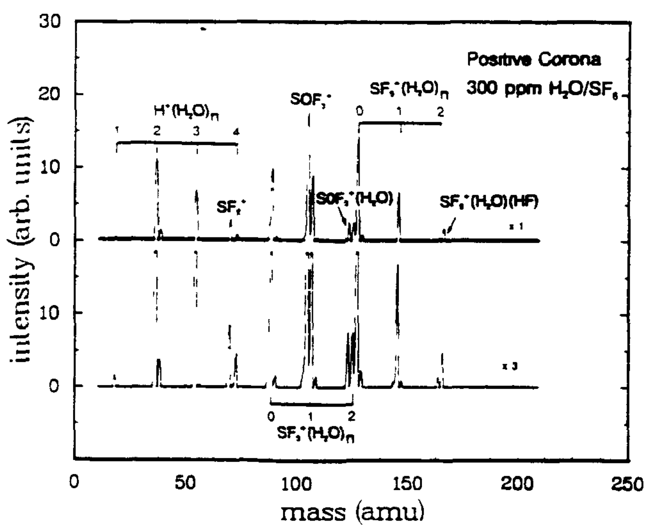

Fig. 5. Positive ion-positive corona mass spectrum for 300 ppm H_2O in SF_6 showing the clusters $H^+(H_2O)_n$, n = 1-4; $SF_5^+(H_2O)_n$, n = 0-2; $SF_3^+(H_2O)_n$, n = 0-2; SOF_3+(H_2O) and $SF_5^+(H_2O)(HF)$ at two sensitivities (x1 and x3).

$F^-(HF)_2$. The HF is believed to be the product of the reaction

$$F + H_2O \rightarrow OH + HF$$

in the discharge.

The ion at m/e = 39 can also be formed by the F^- exchange reaction

$$SF_6^- + HF \rightarrow HF_2^- + SF_5 , \quad (9)$$

since HF has been calculated [9] to have an F^- affinity (2.01 eV) which is higher than that of SF_5 (1.62-1.90 eV).

In Fig. 6 we show a spectrum of 600 ppm H_2O/SF_6. Two cluster series are shown in the figure: $F^-(HF)_n$, n = 0–4, and $OH^-(H_2O)_n$, n = 0–2. The OH^- ion or its companion water clustered ions may be the negative ions responsible for providing free electrons produced by collisional detachment. Recent measurements [10] of collisional detachment cross sections indicate that the thresholds for electron detachment from SF_6^- and SF_5^- are much too high to account for detached electrons.

Negative ions formed as a result of water contamination in SF_6 should be considered, particularly in the case of SF_6 discharges at high pressure. It has been suggested [11], for example, that $O_2^-(H_2O)_n$ might be responsible. However, his ion series was not observed. It should be pointed out, however, that the negative ions observed here are for negative polarity corona. Experiments in which negative ions can be sampled from positive corona are needed. Ions were also observed at m/e = 37 and 57. These could be identified, respectively, either as $F^-(H_2O)$ and $F^-(H_2O)(HF)$ or as $OH^-(HF)$ and $OH^-(HF)_2$. Other ions shown in the figure are SO_2F^- and $SO_2F_2^-$ which are formed from reactions with SO_2 [5].

Conclusions

The addition of water to SF_6 strongly affects the ion chemistry, particularly the positive ion chemistry in SF_6 corona. For positive corona, the water cluster ions $H^+(H_2O)_n$ are formed; while for negative corona, $OH^-(H_2O)_n$ are observed. OH^- and/or its H_2O clusters may be responsible for initiating electrons formed by detachment processes proposed in various models of SF_6 corona. Additional features include $SF_5^+(H_2O)$ whose intensity relative to SF_5^+ correlates well with water content and $F^-(HF)_n$ which indirectly is attributed to water content by the production of HF from reaction of F with H_2O. In dry SF_6 it was found that significant fragmentation occurs in the discharge.

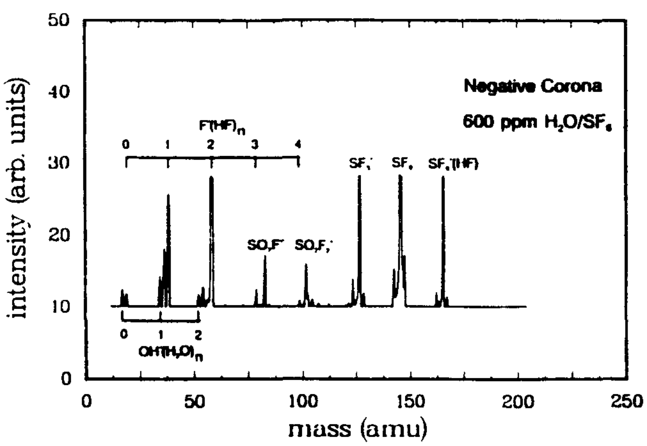

Fig. 6. Negative ion-negative corona mass spectrum for 600 ppm H_2O in SF_6 showing the clusters $F^-(HF)_n$, n = 0–4; $OH^-(H_2O)_n$, n = 0–2; and $SF_6^-(HF)$. See text for discussion of other peaks.

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