COLLISIONAL DECOMPOSITION OF SF₆

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ABSTRACT

investigations [4].

Insulating gas mixtures containing SF₆ have been promoted to serve as replacements for pure SF₆ in order to reduce SF₆ atmospheric emission. It has been argued that some synergism may be achieved by choosing proper buffer gases in mixtures with SF₆ such that the buffer gases efficiently slow down electrons into an energy range where the electron attachment cross section for SF_6 is large. A complete understanding of the dielectric properties of SF₆ mixtures obviously requires information about electron detachment from SF₆ as collisional electron detachment may be the principal of discharge initiation in SF₆ source mixtures. In this paper, we report total cross sections for electron detachment and collision induced dissociation for collisions of SF₆ with N₂ and other proposed admixture gases for collision energies ranging up to a few hundred eV.

INTRODUCTION

Sulfur hexafluoride (SF₆) is widely used as a gaseous dielectric in high-voltage applications due to its extremely large cross section for electron attachment [1,2] and stability with respect to decomposition in subsequent collisions with SF₆[3]. It is also recognized as a greenhouse gas [4] and it has been suggested that a mixture of SF₆ and N₂ might serve as a substitute for pure SF₆ in certain applications which require gaseous dielectrics. The dielectric properties of this mixture have been the subject of recent Collisions of SF_6^- with N_2 which result in the decomposition of SF_6^- are obviously involved in such mixtures when used as gaseous insulators. Cross sections for electron attachment to SF_6^- along with those associated with the decomposition of SF_6^- can partially characterize the ability of the mixture to capture free electrons and keep them bound in subsequent collisions, i.e. the arc-quenching properties of the mixture. The purpose of this paper is to report the measurement of total cross sections for the following types of reactions:

$$\begin{array}{rcl} \mathrm{SF}_6^- + \mathrm{N}_2 & \rightarrow & \mathrm{SF}_6 + \mathrm{e}^- + \mathrm{N}_2 & \sigma_1(\mathrm{E}) \\ & \rightarrow & \mathrm{SF}_5^- + \mathrm{F}^- + \mathrm{N}_2 & \sigma_2(\mathrm{E}) \\ & \rightarrow & \mathrm{SF}_5^- + \mathrm{F}^- + \mathrm{N}_2 & \sigma_3(\mathrm{E}) \end{array} \tag{1}$$

for the laboratory collision energies ranging from 17 eV to 417 eV.

EXPERIMENTAL METHOD

The experimental apparatus and techniques used to measure total cross sections for collisional electron detachment and collision induced dissociation (CID) of SF₆ have been described in detail elsewhere [3], and only pertinent details will be given here. The ion source producing SF₆ used a mixture of 7% SF₆ and 93% Ar at a pressure of about 2 Pa. Thermionically emitted electrons attach to SF₆ and energy analysis of the SF₆⁻ beam shows that SF₆⁻ ions form near the filament where the electron energy is low and electron attachment cross sections are high. The negative ions are extracted from the source, mass analyzed and focused into a cylindrically symmetric electrostatic trapping cell, where $(SF_6)^*$ collides with the target gas at a pressure of ~0.4 μ . Retardation grids are used to ascertain the energy of the primary ion beam and to separate the collision products according to their energy. A magnetic field of about 10 Gauss is used to confine detached electrons which are collected on a small plate parallel to the grids. A typical retardation analysis of CID ions is shown in Fig. 1. The diagram supports the assumption that product ions



Figure 1 Retardation analysis of product ions for collisions of SF_6 with N_2 at $E_{lab} = 120 \text{ eV}$

approximately retain the primary ion's laboratory velocity in the two-step dissociation process as described in Ref.3. In Fig. 1 each subsequent plateau corresponds to the CID ions with higher The first plateau represents energy. complete retardation of F, while the second plateau is due to SF5. At lower collision energies (\$11eV in the center of mass frame), difficulties in determining the cross section for SF₅ production result from large angle elastic and inelastic scattering of the ion beam. The cross sections for σ_1 , σ_2 , and σ_3 are thought to be accurate to within 10%, 15% and 25% respectively. The large uncertainty for σ_3 is due to this large angle elastic/inelastic scattering of SF6.

RESULTS AND DISCUSSION

The measured cross sections for electron detachment and CID of SF_6 by N_2 are presented in Fig. 2 as a function of relative collision



Figure 2 Measured cross sections for electron detachment and CID of SF_6 by N_2 .

energy. Except for the lowest collision energies, CID is the dominant decomposition mechanism for SF₆. The CID channel leading to the production of F has a higher apparent threshold than the CID channel for SF5, which may be attributed to its higher electron affinity. The detachment cross section exhibits a minimum for E ~ 25 eV and increases sharply thereafter. These features are strikingly similar to previous observations for collisions of SF₆ with rare gases [3], as can be seen in Fig. 3 where the electron detachment cross sections for $SF_6 + N_2$ are compared with previous results for the targets He, Ne and Ar. Such target-independent results may be described by a two-step mechanism where collisional excitation of SF₆ by target X is followed by its unimolecular decomposition; viz.,

$$SF_6^{-} + X \rightarrow SF_6^{-*}(U, J_o) + X$$

$$\downarrow e^{-} \text{ or } F^{-} \text{ or } SF_6^{--}$$
(2)

where U is the total internal energy of the excited SF_6 product which is partitioned vibro-



Figure 3 Comparison of the electron detachment cross sections for collisions of SF_6^- with N_2 , He, Ne, and Ar.

rotationally and J_{o} is the rotational quantum number.

The overall dominance of CID over electron detachment for collision energies where all the reaction channels are accessible can be qualitatively understood with the help of the unimolecular decomposition model originally proposed by Klots [5,6]. In this model, the decomposition rates of SF_6^{-*} for channels (1) [i = 1, 2, 3] may be expressed by

$$k_{i}(U_{r}J_{0}) = \frac{\beta_{i}}{h(2J_{0}+1)\rho_{vib}^{(SF_{0})^{*}}(E_{vib})}$$

$$\times \int_{x=0}^{U_{i}=U-U_{0,i}} \rho_{vib}^{product}(x) \sum_{J} \sum_{L} (2J+1)dx,$$
(3)

assuming that $(SF_6)^*$ and polyatomic products of its decomposition can be treated as spherical tops. In the expression above

 ρ_{vib} is the vibrational density of states, $U_{o,i}$ is the threshold internal energy for decomposition into the *i*-th channel, J is the rotational angular momentum of the product spherical top, L is the orbital angular momentum of the products, β_i is the ratio of the symmetry numbers of $(SF_6)^*$ and the product spherical top. The double sum in (3)basically counts the ways the original angular momentum can be partitioned among the products and may be approximated to be $\sim J_0^2$ for computing k2 and k3. The double sum is simply $2J_0 + 1$ for k₁, however, since s-electrons dominate the detachment mechanism. This factor alone is sufficient to account for the relatively small branching ratio observed for detachment. Detailed calculations of (3) using currently available molecular parameters will be presented and discussed during the conference.

SUMMARY

Absolute total cross sections for electron detachment and collision-induced dissociation have been measured for collisions of SF₆ with N₂ for laboratory collision energies from 17 eV to 417 eV. Electron detachment cross sections are below 4.5 Å² with minimum of ~1 Å² at E ~ 20 eV. These cross sections are higher than those for the SF_6 target [3] and can partly account for lower dielectric properties of a SF₆/N₂ mixture compared to those of pure SF₆. CID processes provide the dominant destruction mechanism for SF_6 with absolute cross sections approaching 35Å² at higher energies. The decomposition cross sections of SF_6^- in collisions with N_2 are similar to those observed for rare gas targets. The target-independent features of SF6 decomposition can be qualitatively explained using a two-step model in which collisional decomposition is followed by unimolecular decomposition.

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