# Collisional decomposition of the sulfur hexaflouride anion $(SF_6)$

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Insulating gas mixtures containing SF<sub>6</sub> have been promoted to serve as replacements for pure SF<sub>6</sub> in order to reduce SF<sub>6</sub> atmospheric emission. It has been argued that some synergism may be achieved by choosing proper buffer gases in mixtures with SF<sub>6</sub> such that the buffer gases efficiently slow down electrons into an energy range where the electron attachment cross section for SF<sub>6</sub> is large. A complete understanding of the dielectric properties of SF<sub>6</sub> mixtures obviously requires information about electron detachment from SF<sub>6</sub><sup>-</sup> as collisional electron detachment may be the principal source of discharge initiation in SF<sub>6</sub> mixtures. In this paper, we report total cross-section measurements for electron detachment and collision induced dissociation for collisions of SF<sub>6</sub><sup>-</sup> with N<sub>2</sub> for collision energies ranging up to a few hundred eV. The experimental results are analyzed using a two-step collision model where the unimolecular decomposition of collisionally excited SF<sub>6</sub><sup>-</sup> ions is described in a statistical framework. © 2001 American Institute of Physics. [DOI: 10.1063/1.1380692]

## I. INTRODUCTION

Sulfur hexafluoride (SF<sub>6</sub>) is widely used as a gaseous dielectric in high-voltage applications due to its extremely large cross section for electron attachment<sup>1-3</sup> and stability of  $SF_6^-$  with respect to decomposition in subsequent collisions with SF<sub>6</sub>.<sup>4</sup> It is also recognized as a potent greenhouse gas and it has been suggested that a mixture of SF<sub>6</sub> and N<sub>2</sub> might serve as a substitute for pure SF<sub>6</sub> in certain applications which require gaseous dielectrics.5,6 Even with a very low SF<sub>6</sub> content, a SF<sub>6</sub>/N<sub>2</sub> mixture exhibits many of the desirable properties of SF<sub>6</sub> as a gaseous dielectric. It has been suggested that this mixture may constitute a synergistic combination: The buffer gas (N2) serves to cool energetic electrons into the low-energy region where the electronegative gas (SF<sub>6</sub>) captures them with a remarkably high crosssection, thereby inhibiting the buildup of free electrons that could cause ionization leading to electrical breakdown. The dielectric properties of this mixture have been the subject of numerous recent investigations.5,6

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 arcquenching properties of the mixture, viz., the ability of the mixture to capture free electrons and keep them bound in subsequent collisions. The collisional decomposition of  $SF_6^$ will also be an important reaction pathway leading to creation of chemical by-products and thus needs to be understood in order to fully characterize the dielectric and chemical stability of  $SF_6/N_2$  mixtures. The purpose of this paper is to report the measurement of total cross sections,  $\sigma_i$  (*i*=1,2,3), for the following three least endothermic reactions:

$$SF_{6}^{-} + N_{2} \rightarrow SF_{6} + e^{-} + N_{2}; Q_{1} = -1.06 \text{ eV}$$
  
$$\rightarrow SF_{5}^{-} + F + N_{2}; Q_{2} = -1.18 \text{ eV}$$
  
$$\rightarrow SF_{5} + F^{-} + N_{2}; Q_{3} = -1.58 \text{ eV}, \qquad (1)$$

for the laboratory collision energies,  $E_{\text{lab}}$ , ranging from 17 eV to 417 eV. The threshold energies given in Eq. (1) for each channel,  $Q_i$ , are for ground state reactants and products.<sup>7,8</sup>

#### **II. EXPERIMENTAL METHOD**

The experimental apparatus and techniques used to measure total cross sections for collisional electron detachment and collision induced dissociation (CID) of SF<sub>6</sub> have been described in detail elsewhere,<sup>4</sup> and only the pertinent details will be given here. The ion source producing  $SF_6^-$  used a mixture of 7% SF<sub>6</sub> and 93% Ar at a pressure of about 2 Pa. Thermionically emitted electrons attach to SF<sub>6</sub> and energy analysis of the resulting  $SF_6^-$  beam shows that  $SF_6^-$  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 the molecular anion collides with  $N_2$  at a pressure of  $\sim 5$  $\times 10^{-2}$  Pa. Retardation grids are used to ascertain the energy of the primary ion beam and to separate the collision products according to their energy. A longitudinal magnetic field of about 10 G is used to isolate and confine detached electrons which are collected on a small plate parallel to the grids. A typical retardation analysis of CID ions for collisions of SF<sub>6</sub> with N<sub>2</sub> at  $E_{lab} = 120 \text{ eV}$  is shown in Fig. 1. The

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FIG. 1. Retardation analysis of product ions for collisions of SF<sub>6</sub><sup>-</sup> with N<sub>2</sub> at  $E_{\rm lab}$  = 120 eV. The slight decrease for V>110 volts is unavoidable due to subtracting "gas in" from "gas out" signals, as the former contain some nonreactive inelastic scattering.

diagram supports the assumption that product ions approximately retain the primary ion's laboratory velocity in the dissociation process as described in Ref. 4. In Fig. 1 each subsequent plateau corresponds to the CID ions with higher energy. The first plateau represents complete retardation of  $F^-$ , while the second plateau is due to  $SF_5^-$ . At lower collision energies ( $\leq 11 \text{ eV}$  in the center of mass frame), difficulties in determining the cross section for  $SF_5^-$  production result from large angle elastic and inelastic scattering of the primary ion beam. The cross sections for  $\sigma_1$ ,  $\sigma_2$ , and  $\sigma_3$  are thought to be accurate to within 10%, 25%, and 15%, respectively. The large uncertainty for  $\sigma_2$  is due to this large angle elastic/inelastic scattering of  $SF_6^-$ .

### III. 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 energy,  $E_{rel}$ . It is interesting to observe that although electron detachment has the lowest threshold energy for decomposition, CID is the dominant decomposition mechanism for the anion, except for the lowest collision en-



FIG. 2. The cross sections for electron detachment and CID of  $SF_6^-$  by N<sub>2</sub> as a function of  $E_{rel}$ .

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FIG. 3. Comparison of the electron detachment cross sections for collisions of  $SF_6^-$  with N<sub>2</sub>, He, Ne, and Ar.

ergies. The CID channel leading to the production of F<sup>-</sup> has a higher energetic threshold than that for SF<sub>5</sub><sup>-</sup>, which may be attributed to the higher electron affinity of SF<sub>5</sub>. The electron detachment cross section exhibits a minimum for  $E_{rel}$ ~25 eV and increases sharply thereafter. These features are strikingly similar to previous observations for collisions of SF<sub>6</sub><sup>-</sup> with rare gases,<sup>4</sup> as can be seen in Fig. 3, where the electron detachment cross sections for SF<sub>6</sub><sup>-</sup> +N<sub>2</sub> are shown along with previous results for the targets He, Ne and Ar. Such target-independent results are often described by a twostep mechanism where collisional excitation of SF<sub>6</sub><sup>-</sup> by the target X is followed by its unimolecular decomposition; viz.,

$$SF_6^- + X \rightarrow SF_6^{-*}(U, J_0) + X$$
  
$$\not \rightarrow e^- \text{ or } F^- \text{ or } SF_5^-, \qquad (2)$$

where U is the total internal energy of the unstable, excited  $SF_6^{-*}$  product which is partitioned rovibrationally and  $J_0$  is the rotational quantum number, indicating that portion of U which is rotational energy.

The overall dominance of CID over electron detachment for collision energies, where all the reaction channels are energetically accessible, can be qualitatively understood with the help of the unimolecular decomposition model originally proposed by Klots.<sup>9,10</sup> In this model, the decomposition rates of  $SF_6^{-*}$  for products given in Eq. (1) may be expressed by

$$k_{i}(U,J_{0}) = \frac{\beta_{i}}{h(2J_{0}+1)\rho_{\text{vib}}^{(\text{SF}_{6}^{-})*}(E_{\text{vib}})}$$
$$\times \int_{\varepsilon=0}^{U_{i}=U-Q_{i}} \rho_{\text{vib}}^{\text{product}}(\varepsilon) \sum_{J} \sum_{L} (2J+1)d\varepsilon,$$
(3)

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

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above  $\rho_{\rm vib}$  is the vibrational density of states, J is the rotational angular momentum of the product spherical top, L is the orbital angular momentum of the products,  $\beta_i$  is the ratio of the symmetry numbers of  $(SF_6^-)^*$  and the product spherical top. The vibrational density of states can be approximated<sup>11</sup> as

$$\rho_{\rm vib}(\varepsilon) = \frac{(\varepsilon + \varepsilon_0)^{s-1}}{(s-1)! \prod_{i=1}^{s} h \nu_i},\tag{4}$$

where  $\varepsilon_0$  is the zero-point energy,  $\varepsilon$  is the energy above the zero-point level, s is the number of vibrational degrees of freedom, and  $\nu_i$  are the vibrational frequencies. It is not necessary to consider excited electronic states of the anion in this treatment as, for a given U, the vibrational density of states of any excited electronic state will be negligible compared to that for the ground state.

To evaluate Eq. (4), the values of vibrational frequencies  $\nu_i$  for SF<sub>6</sub><sup>-</sup>, SF<sub>6</sub>, SF<sub>5</sub><sup>-</sup>, and SF<sub>5</sub> were taken from recent calculations by Lugez *et al.*<sup>12</sup> Not all of these vibrational frequencies are known experimentally. Where both the calculated and experimentally determined frequencies exist (SF<sub>6</sub>, for example), their differences are in the range of 10%. It is important to point out that a change of this magnitude for  $\nu_i$ does not alter the conclusions which arise from these calculations in any substantive manner.

The internal energy, U, of  $(SF_6^-)^*$  was assumed to partition equally among its three rotational and fifteen vibrational degrees of freedom. The initial angular momentum quantum number,  $J_0$ , was then calculated according to

$$E_{\rm rot} = BJ(J+1) \tag{5}$$

for a spherical top where B is the rotational constant. The threshold energies,  $Q_i$ , for electron detachment and CID into  $SF_5^-$  or  $F^-$  given in Eq. (1) were used in the calculation. There exist some uncertainties about these threshold energies, but there is a general agreement on the order in which these values follow.<sup>7,8</sup>

The restrictions on the product angular momentum quantum numbers J and L in Eq. (3) were determined as follows: For electron detachment, s-electrons dominate the detachment mechanism or L=0 and  $J=J_0$ . For CID channels 2 and 3, once a value of  $\varepsilon$  is chosen, the rotational energy,  $E_{rot}$ of the product spherical top can range from zero to  $U-Q_i - \varepsilon$ . The range of J is then calculated according to Eq. (5). Two factors determine the range of L in Eq. (3): The triangle rule  $|J-J_0| \le L \le J+J_0$  and the Langevin orbiting restriction<sup>9</sup>

$$L_{\max}(L_{\max}+1) = \gamma (U-Q_i - \varepsilon - E_{rot}).$$

Here,

$$\gamma = 2^{3/2} \mu e \alpha^{1/2} / \hbar^2$$

where  $\mu$  is the reduced mass of the CID products, and  $\alpha$  is the polarizability of the neutral product. In these calculations we assumed that SF<sub>5</sub><sup>-</sup>, when its internal energy is high enough, would itself decompose. The decomposition channel for SF<sub>5</sub><sup>-</sup>, which has the lowest threshold energy, is F<sup>-</sup>+SF<sub>4</sub> (1.1 eV).<sup>12</sup> The threshold energies for decomposing into SF<sub>4</sub><sup>-</sup>+F (3.0 eV) and e<sup>-</sup>+SF<sub>5</sub> (3.8 eV)<sup>12</sup> are significantly



FIG. 4. Calculated decomposition rates,  $k_1$ ,  $k_2^{\text{eff}}$ , and  $k_3^{\text{eff}}$ , are plotted as a function of the internal energy, U, of  $(SF_6^-)^*$ .

higher, and, as will become clear later in this paper, they are beyond the energy range of the present treatment. The decomposition rate,  $k_4$ , for  $SF_5^- \rightarrow F^- + SF_4$  was calculated using the same statistical model, with vibrational frequencies also taken from the work of Lugez *et al.*<sup>12</sup> The decomposition of  $SF_5^-$  produces a source for  $F^-$  and a sink for  $SF_5^-$ . The production rate of  $F^-$  via  $SF_5^-$  is governed by the rate of the slower, rate-determining step of the overall reaction, with a characteristic time  $\tau = 1/k_2 + 1/k_4$ . The combined effective rate for  $F^-$  production from  $(SF_6^-)^*$  is then  $k_3^{\text{eff}} = k_3 + 1/\tau$ , and for  $SF_5^-$  production, it is  $k_2^{\text{eff}} = k_2 - 1/\tau$ . Of course,  $k_1^{\text{eff}} = k_1$ , as we have considered no additional source or sink of electrons.

The resulting decomposition rates for  $(SF_6^-)^*$  are presented in Fig. 4. The main features which can be immediately observed are as follows. The decomposition rates for the three channels of reaction [Eq. (1)] onset in the order of their internal threshold energies. However, the rates for the CID channels initially rise more steeply with increasing internal energy of  $SF_6^-$  than the detachment rate, which can be attributed to the larger phase space for the angular momenta of the CID products than that for the detachment products. The production of  $SF_5^-$  becomes the dominant decay mechanism as U increases above 1.5 eV until it reaches around 2.3 eV, where the secondary decomposition rate of  $SF_5^-$  rises so steeply that  $F^-$  quickly becomes the dominant product ion.

To facilitate comparison between the decomposition rates of  $(SF_6^-)^*$  and the decomposition cross sections in collisions of  $SF_6^-$  with N<sub>2</sub>, we present the calculated branching ratios  $k_i^{\text{eff}}/(\Sigma k_i^{\text{eff}})$  as a function of U in Fig. 5(a) along with the measured branching ratios  $\sigma_i / \Sigma(\sigma_i)$  as a function of the relative collision energy,  $E_{\text{rel}}$ , in Fig. 5(b). As can be seen in the figure, the overall features of the calculated branching ratios resemble the experimentally determined branching ratios; both show that there are three distinct energy regions with different dominant product ions. This comparison clearly shows that the model calculation can be used to better understand the experimental results. As the collision energy increases, more translational energy is converted into the internal rovibrational excitation energy of  $(SF_6^-)^*$ . The first

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FIG. 5. (a) Calculated branching ratios  $k_i^{\rm eff}/(\Sigma k_i^{\rm eff})$  as a function of U; (b) measured branching ratios  $\sigma_i/\Sigma(\sigma_i)$  as a function of  $E_{\rm rel}$ .

energetically allowed decomposition channel for  $(SF_6^-)^*$  is the electron detachment. The detachment probability quickly decreases, however, as the collision energy increases because the rate for the competing CID channel leading to  $SF_5^-+F$ rises faster. As U is increased further,  $SF_5$  becomes the dominant product ion in the intermediate energy region. The calculation also reveals that the decomposition rate for  $SF_5^- \rightarrow F + SF_4$  rises steeply as the internal energy increases above its decomposition threshold and this secondary process may, in fact, be the main source of F<sup>-</sup> ions detected in collisions of SF<sub>6</sub> with N<sub>2</sub>. The statistical model cannot, however, explain why the detachment cross section,  $\sigma_1(E_{\rm rel})$ , rises for  $E_{\rm rel} \ge 30 \, {\rm eV}$ . This increase observed for  $\sigma_1(E_{\rm rel})$  is undoubtedly due to a competing, direct detachment mechanism which is distinct from that which follows collisional excitation of SF<sub>6</sub>.

The results of Fig. 5 suggest that, to a rough approximation, a mapping of  $U(E_{rel})$  might be given by  $U(E_{rel}) \approx [1 + \log_{10} (E_{rel}/eV)]$  eV. It is clear from Fig. 4 that any primary SF<sub>6</sub><sup>-</sup> ions formed by attaching electrons with energies less than 0.2 eV will, although metastable, clearly survive their trip from the source to the collision region, a transit requiring about 10  $\mu$ sec. Hence the mean internal energy,  $U^0$ , of the SF<sub>6</sub><sup>-</sup> ion *prior* to its collision with N<sub>2</sub> is fairly well-defined and will be slightly in excess of the electron affinity of SF<sub>6</sub>. The collision then provides the additional excitation,  $U^{add}$  $\approx [\log_{10}(E_{rel}/eV)]$  eV, with  $U = U^0 + U^{add}$ . Obviously there Champion et al.

is no simple, unique correspondence between  $E_{rel}$  and U; the mapping is clearly much more complicated than given above. Nevertheless, it is interesting to note that one can characterize certain aspects of an extremely complicated inelastic collision with such a simple model.

## **IV. SUMMARY**

Absolute total cross sections for electron detachment and collision-induced dissociation have been measured for collisions of SF<sub>6</sub> with N<sub>2</sub> for laboratory collision energies from 17 eV to 417 eV. Electron detachment cross sections are below 4.5 Å<sup>2</sup> with minimum of  $\sim 1$  Å<sup>2</sup> at  $E \sim 20$  eV. These cross sections are higher than those for the SF<sub>6</sub> target<sup>4</sup> and can partly account for lower dielectric properties of a  $SF_6/N_2$  mixture compared to those of pure  $SF_6$ . Collision induced dissociation processes provide the dominant destruction mechanism for SF<sub>6</sub> with absolute cross sections approaching 35 Å<sup>2</sup> at higher energies. The decomposition cross sections of  $SF_6^-$  in collisions with N<sub>2</sub> are similar to those observed for rare gas targets. The target-independent features of  $SF_6^-$  decomposition can be qualitatively explained using a two-step model in which collisional decomposition is followed by unimolecular decomposition. This model shows that the dominance of CID processes result from the larger phase space for the CID channels than the electron detachment. The model calculation also suggests that the main source of F<sup>-</sup> ions detected in collisions of SF<sub>6</sub><sup>-</sup> with N<sub>2</sub> may result from subsequent decomposition of excited SF<sub>5</sub>.

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