Collisional electron detachment and decomposition rates of SF_6^-, SF_5^-, and F^- in SF_6: Implications for ion transport and electrical discharges

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(Received 9 February 1989; accepted 1 May 1989)

Measured cross sections for prompt collisional detachment and decomposition of SF_6^-, SF_5^-, and F^- in SF_6 reported in the preceding companion paper are used to calculate detachment coefficients and ion-conversion reaction coefficients as functions of electric field-to-gas density ratio (E/N) for ion drift in SF_6. Analysis from a model presented here using these coefficients suggests that prompt electron detachment from SF_6^- and SF_5^- in SF_6 are insignificant processes in such ion-drift experiments. Calculated rates for ion-conversion processes indicate the necessity to: (1) reexamine the previously measured rates in SF_6 from drift-tube experiments, and (2) use ion kinetic-energy distributions with larger high-energy tails than the standard distributions assumed in earlier calculations. The calculated detachment and reaction coefficients are used in a model which invokes detachment from long-lived energetically unstable states of collisionally excited SF_6^- to explain the pressure dependence of previously measured detachment coefficients and the high detachment thresholds implied by analysis of electrical-breakdown probability data for SF_6. Consistent with the interpretation of results from earlier work, the model indicates that at high pressure, measured detachment coefficients depend primarily upon rates for ion conversion and prompt collisional detachment from F^-

I. INTRODUCTION

The direct experimental determination of the collisional electron-detachment cross sections for SF_6^- and other negative ions formed in SF_6 is important because of the relevance of these processes as electron release mechanisms in electrical discharges.[1,2] A knowledge of the energy dependence of the collisional-detachment cross sections along with an assumed particle speed distribution function allows one to estimate the detachment coefficients needed for electrical-discharge modeling in SF_6. It is especially important, for example, to know the threshold energies for the detachment processes. Previous analyses[1] of discharge or breakdown-inception data for SF_6 indicate collisional electron-detachment thresholds in the range from 5 to 8 eV. Although not particularly relevant to the present discussion, it should be pointed out that calculated potential-energy curves predict threshold values for SF_6^- photodetachment between 3 and 4 eV.[3,4] All of these values are significantly higher than the reported electron affinity of SF_6^- (~ 1 eV).[5]

Collisional electron-detachment coefficients determined from low-pressure, uniform-field drift-tube measurements[6,7] lie significantly above the coefficients estimated from electrical-breakdown initiation data[1] and exhibit an unexplained inverse-pressure dependence. There is also evidence from uniform-field drift-tube experiments of rapid ion-conversion processes in SF_6 that can compete with electron-detachment processes.[6,8–13] However, the exact nature of these processes has not previously been determined.

In this paper we use the measured collisional electron-detachment and collisional-induced dissociation cross sections for SF_6^-, SF_5^-, and F^- on SF_6 presented in the preceding companion paper[14] to calculate electron-detachment and ion-conversion reaction coefficients as functions of electric field-to-gas density ratios (E/N) for the reactions listed in Table I. We discuss the relevance of these results to the interpretation of data from uniform-field drift-tube measurements and measurements of electrical-discharge initiation probabilities.

II. CROSS SECTION DATA

The experimental apparatus and techniques used to obtain the cross section data are discussed in detail in the preceding companion paper.[14] The measured energy dependencies of the collisional electron-detachment cross sections $\sigma_i(\epsilon_{\text{c.m.}})$ for SF_6^-, SF_5^-, and F^- on an SF_6 target are reshown in Fig. 1 where $\epsilon_{\text{c.m.}}$ is the relative (center-of-mass)

TABLE I. Collisional processes for which cross sections have been presented in the present work.

Cross section (σ_i)	Reaction
σ_1	$SF_6^- + SF_6 \rightarrow e^- + SF_6 + SF_6$
σ_2	$SF_5^- + SF_6 \rightarrow e^- + SF_5 + SF_6$
σ_3	$F^- + SF_6 \rightarrow e^- + F + SF_6$
σ_4	$SF_6^- + SF_6 \rightarrow F^- + SF_5 + SF_6$
σ_5	$SF_5^- + SF_6 \rightarrow F^- + SF_4 + SF_6$
σ_6	$SF_6^- + SF_6 \rightarrow SF_5^- + F + SF_6$
σ_7	$SF_6^- + SF_6 \rightarrow$ charge-transfer products $+ SF_6$
σ_8	$SF_5^- + SF_6 \rightarrow$ charge-transfer products $+ SF_5$
σ_9	$F^- + SF_6 \rightarrow F + SF_6^-$ (see Ref. 16)

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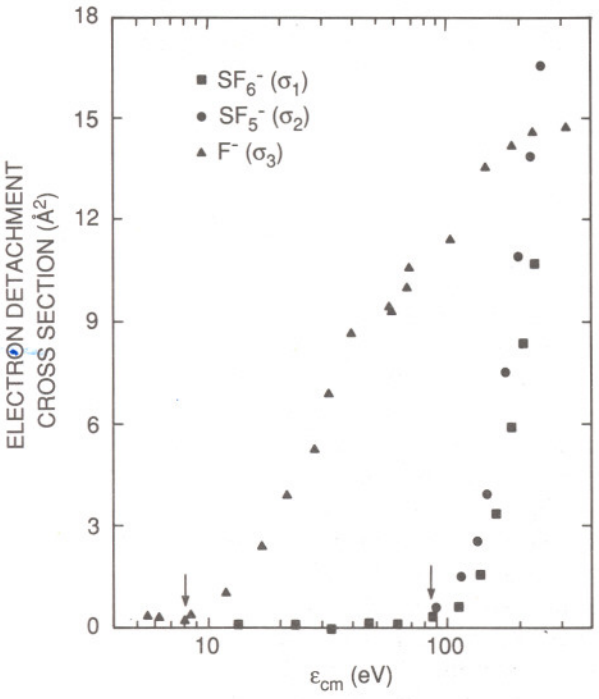

FIG. 1. Collisional electron-detachment cross sections for F^-, SF_5^-, and SF_6^- on SF_6 target gas as a function of center-of-mass energy.

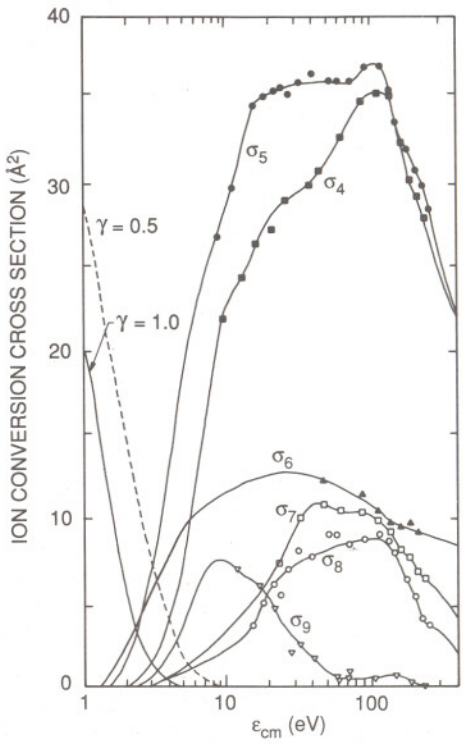

FIG. 2. Measured cross sections for collision-induced ion-conversion processes in SF_6 target gas: (●) F^- from SF_5^-; (■) F^- from SF_6^-; (▲) SF_5^- from SF_6^-; (○) ions due to charge-transfer reactions of SF_5^-; (□) ions due to charge-transfer reactions of SF_6^-; and (∇) ions due to charge-transfer reactions of F^-. The two exponentially decaying curves on the left side of the figure represent the kinetic-energy distribution of Eq. (5) for $\gamma = 1.0$ and $\gamma = 0.5$ scaled relative to each other.

collision energy. Apparent thresholds at 90 eV for SF_6^- and SF_5^-, and at 8 eV for F^-, are marked by vertical arrows. With the present experimental limitations, it is not possible to demonstrate that $\sigma_i(\epsilon_{c.m.})$ is actually zero for energies below the marked thresholds.[14] However, this assumption is used here in computing detachment rates.[15] The experiments place only upper limits on the measured detachment cross sections for energies below the indicated thresholds. The consequences of assuming nonzero cross sections at lower energies will be discussed later.

Cross sections for the ion-conversion processes listed in Table I are reshown in Fig. 2 together with extrapolations down to the thresholds used in the calculation of corresponding rate coefficients. The bases for these extrapolations are discussed later in the paper. The solid symbols indicate cross sections due to collisional-induced-dissociation (CID) processes, and the open symbols indicate cross sections for charge-transfer processes (including charge-transfer decomposition). There is evidence that the charge-transfer process involving SF_6^- on SF_6 is predominately dissociative,[17,18] and that charge transfer involving F^- on SF_6 may lead to both SF_6^- and SF_5^- (Refs. 6 and 17).

III. CALCULATIONS

The analysis of rates for chemical processes in drift tubes or electrical discharges requires expressing inelastic-collision probabilities in terms of rate coefficients rather than cross sections. For a process where the projectiles have a velocity distribution $f(v)$, the rate coefficient k becomes[19]

$$k = \int_0^\infty \sigma(v) v f(v) dv \,, \tag{1}$$

where $\sigma(v)$ is the velocity dependent cross section for the process and $f(v)$ is subject to the normalization

$$\int_0^\infty f(v) dv = 1 \,. \tag{2}$$

For measurements where charged particles are accelerated in a gas by an electric field, the reaction coefficient κ is defined as the reaction probability per unit length in the direction of the electric field, and is related to the rate coefficient by

$$\frac{\kappa}{N} = \frac{k}{v_d} \,, \tag{3}$$

where N is the target-gas number density and v_d is the charged particle drift velocity. For the special case of collisional electron detachment from a negative ion, the reaction coefficient is referred to as the detachment coefficient δ (i.e., $\kappa/N = \delta/N$ for collisional electron detachment).

Reaction coefficients for detachment and ion-conversion processes involving SF_6^-, SF_5^-, and F^- in SF_6 can be derived from the measured cross sections $\sigma_i(\epsilon_{c.m.})$ presented in Figs. 1 and 2 from

$$\frac{\kappa_i}{N} = \frac{1}{m v_d} \int_0^\infty \sigma_i(\epsilon_L) f(\epsilon_L) d\epsilon_L \,, \tag{4}$$

where ϵ_L is the projectile energy in the lab frame, m is the mass of the negative ion, and $f(\epsilon_L)$ and $\sigma(\epsilon_L)$ are the ion kinetic-energy distribution and the process cross sections,

respectively. The ion drift velocity is assumed to be given by $v_d = \mu E$, where μ is the ion mobility and E is the applied electric-field strength.

It should be noted that the determination of reaction coefficients from collisional cross sections suffers from certain difficulties, the greatest arising from the assumed form of the ion kinetic-energy distribution $f(\epsilon_L)$.[20] While determination of ion kinetic-energy distributions has received considerable theoretical[21] and experimental[22] attention, the theoretical work is hampered by the lack of detailed ion–atom (or molecule) potential-energy surfaces and the experimental work suffers from a lack of reliability.[20] Accurate direct measurements of ion-velocity distributions have been demonstrated in recent optical-probing experiments,[23] but to date no experimental data are available for the kinetic-energy distributions of SF_6^-, SF_5^-, or F^- in SF_6.

In general, experimental work has indicated that ions with masses less than or equal to that of the molecules of the gas in which they are moving exhibit kinetic-energy distributions with high-energy tails.[20,24] Differences in the distributions at high energies in Eq. (4) will obviously have a large effect upon the calculated reaction coefficients derived from cross sections with threshold energies considerably in excess of the average ion kinetic energies.

An example of the large differences in calculated values of reaction coefficients which can occur when different energy distributions are assumed is shown in Fig. 3, where the collisional-detachment coefficient for F^- in SF_6 (δ_3) has been calculated as a function of E/N using the cross section data (σ_3) from Fig. 1 and several different indicated energy distributions. The solid lines in Fig. 3 represents detachment coefficients calculated using the kinetic-energy distribution of Kagan and Perel,[1,25]

$$f(\epsilon_L) = \frac{\sqrt{6\gamma}}{\pi v_d} \exp\left(\frac{-\gamma\epsilon_L}{\pi m v_d^2}\right), \tag{5}$$

which assumes that charge exchange is the dominant ion–molecule interaction. For the standard Kagan and Perel distribution, $\gamma = 1.0$. However, as will be discussed later, better agreement between ion-conversion reaction coefficients calculated here and those from analysis of drift-tube results is obtained by assuming $\gamma = 0.5$ which introduces a larger high-energy tail in the distribution.

The dashed line in Fig. 3 was obtained using a Maxwellian speed distribution[1] of the form

$$f(\epsilon_L) = 3\sqrt{\frac{3m}{\pi}} \frac{\epsilon_L}{\bar{\epsilon}^{3/2}} \exp\left(\frac{-3\epsilon_L}{2\bar{\epsilon}}\right), \tag{6}$$

where the mean energy of the ion in the lab frame is given by[26]

$$\bar{\epsilon} = \frac{3}{2}kT + \frac{m}{2}v_d^2 + \frac{M}{2}v_d^2 \tag{7}$$

and M is the mass of the collision-gas molecules. This distribution has been used previously when analyzing discharge-inception data[1] and is similar to a strongly anisotropic velocity distribution derived by Skullerud[27] for ions drifting in a gas composed of molecules of the same mass as the ions under high electric fields.

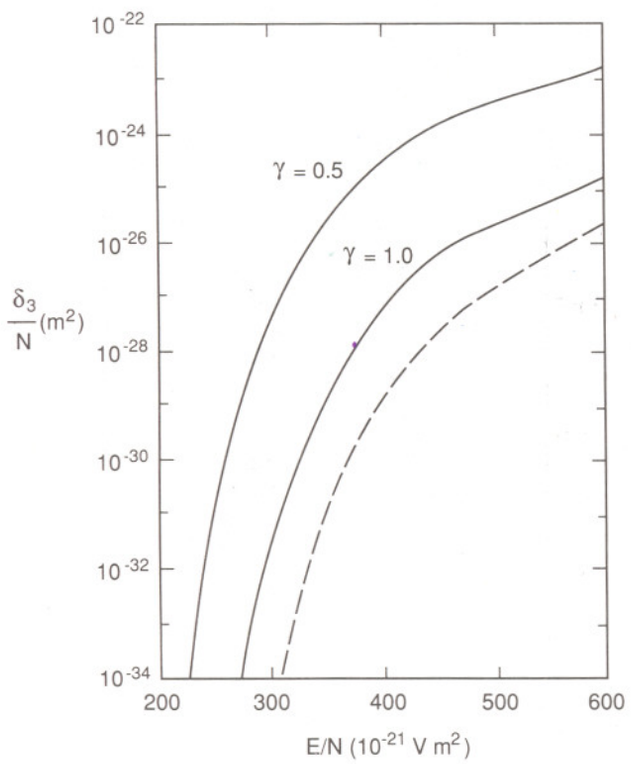

FIG. 3. Calculated collisional electron-detachment coefficients for F^- in SF_6 gas using Eq. (4) and $\sigma_3(\epsilon_L)$, and assuming different ion kinetic-energy distributions: (—) Kagan and Perel; (- - -) Maxwellian.

In addition to the uncertainty associated with the assumed distribution function, another source of uncertainty in deriving reaction coefficients from cross-section data is the choice of experimentally determined values of ion mobilities (μ). Several previous mobility measurements[28–31] for SF_6^- and SF_5^- in SF_6 are not in complete agreement. The most current measurements[31] are in agreement with a previous study by Brand and Jungblut[28] which indicates that the mobilities decrease as E/N increases for electric-field strengths above the critical value at which the ionization and electron-attachment rates in SF_6 are equal. Earlier measured data compiled by Morrow[29] indicate that the mobilities may continue to increase as E/N increases even for E/N values greater than the critical value. However, differences in calculated reaction coefficients using different mobilities are significantly smaller than the differences due to the use of different energy distributions. For the remainder of this paper, the mobilities used for SF_6^- and SF_5^- are those reported by Brand and Jungblut,[28] and for F^-, the values of Nakamura.[31]

IV. RESULTS

A. Collisional-detachment reaction coefficients

The extremely high apparent thresholds observed in the cross section data for prompt electron detachment from SF_6^- and SF_5^- in SF_6 indicate that the corresponding detachment coefficients will be very small. One can estimate the coefficients for these processes by assuming that the cross section rises abruptly from zero at the observed threshold energy (ϵ_0), i.e.,

$$\sigma(\epsilon_L) = \begin{cases} \sigma_0, & \epsilon_L > \epsilon_0 \\ 0, & \epsilon_L < \epsilon_0 \end{cases}, \tag{8}$$

where ϵ_0 is the threshold energy in the lab frame. Assuming that $f(\epsilon_L)$ is a standard Kagan and Perel distribution (i.e., $\gamma = 1$) in Eq. (4) gives

$$\frac{\delta}{N} = \sigma_0 \sqrt{\frac{2}{3}} \exp\left(\frac{-3\epsilon_0}{\pi\mu v_d^2}\right). \tag{9}$$

Clearly, any reasonable value of σ_0 will lead to a completely negligible value of δ/N if the apparent high-energy thresholds in Fig. 1 (i.e., $\epsilon_0 \simeq 180$ eV) are invoked. Thus one must conclude that prompt collisional electron-detachment processes for SF_6^- (and SF_5^-) in SF_6 cannot be significant reactions for production of electrons in discharge-inception processes, if, in fact, Eq. (8) is valid and ϵ_0 is large. It should be noted that this conclusion is independent of the assumed kinetic-energy distribution or mobility data used.

It is clear from Fig. 3, however, that collisional electron detachment from F^- in SF_6 is a significant process, thus suggesting that previously observed electron-detachment processes due to motion of negative ions in SF_6 are most likely from F^-. This agrees with earlier works[32] which indicated that detachment was predominantly from F^-, and also with recent reanalysis of pulsed-electron avalanche experiments.[13,33] In fact, the observed threshold for electron detachment from F^- in SF_6 near 8 eV is consistent with the hypothesized thresholds predicted by discharge-inception experiments.[1,2]

The conclusions drawn above depend upon the assumption made in Eq. (8) that $\sigma(\epsilon_L) = 0$ at energies below ϵ_0. If one assumes that $\sigma(\epsilon_L) = 0.1$ Å^2 (i.e., the experimental uncertainty) for energies which extend down to the thermodynamic threshold for electron detachment, then detachment coefficients for SF_6^- and SF_5^- are found to be of the same order of magnitude as those determined by drift-tube experiments. However, detachment coefficients derived with such an assumption are not compatible with previous pressure studies[6,7]; this will be discussed later.

B. Ion-conversion reaction coefficients

In order to calculate the reaction coefficients for the ion-conversion processes listed in Table I, it is necessary to extrapolate the measured cross sections down to assumed thresholds at lower energies. The extrapolations used for the subsequent calculations are shown in Fig. 2. These extrapolations were chosen to agree with known thermodynamic thresholds and to minimize the discrepancies with previously determined reaction coefficients as discussed below. The thresholds for production of F^- from SF_6^- and SF_5^- (σ_4 and σ_5) were determined to be 2.0 and 1.5 eV, respectively, by using the observed thresholds from collisions of SF_6^- and SF_5^- with the rare gas targets presented in the preceding paper.[14] The cross sections for SF_5^- production[34] (σ_6) from SF_6^- were extrapolated down to the thermodynamic threshold of 1.35 eV. For the charge-transfer reaction involving F^- and SF_6, the cross sections were extrapolated down to the thermodynamic threshold of 2.25 eV under the assumption that the primary product is SF_6^- (see Ref. 16). The other charge-transfer cross sections (σ_7 and σ_8) were both extrapolated down to a threshold near 3 eV which corresponds to the thermodynamic threshold for a symmetric charge transfer between SF_6^- and SF_6 as suggested by Hay.[4] There is a large uncertainty in these last assumed thresholds since the identity of the charge-transfer products in these processes are indistinguishable in the present experiment.

The calculated reaction coefficients for processes 6, 5, and 9 (of Table I) are shown in Figs. 4, 5, and 6, respectively, along with the reaction coefficients for the same reactions as determined by previous drift-tube experiments. The solid lines represent the coefficients calculated using the standard Kagan and Perel distribution (i.e., $\gamma = 1$) shown in Eq. (5). Note that these calculated reaction coefficients all fall substantially below those determined previously despite the fact that the extrapolated thresholds for these cross sections were all assumed to be thermodynamic thresholds. Any reasonable change in the assumptions concerning the reaction thresholds or the behavior of the cross sections near thresholds would necessarily cause the reaction coefficients to be even smaller, thus implying that the discrepancies cannot be resolved by changing the assumed cross section thresholds or extrapolations.

Despite the fact that the Kagan and Perel distribution produces the largest coefficients of any of the commonly used kinetic-energy distributions, better agreement can be obtained between our calculated coefficients and those from previous experiments if one assumes that the kinetic-energy distribution has a longer high-energy tail, in agreement with the previous discussion of kinetic-energy distributions.[20–24]

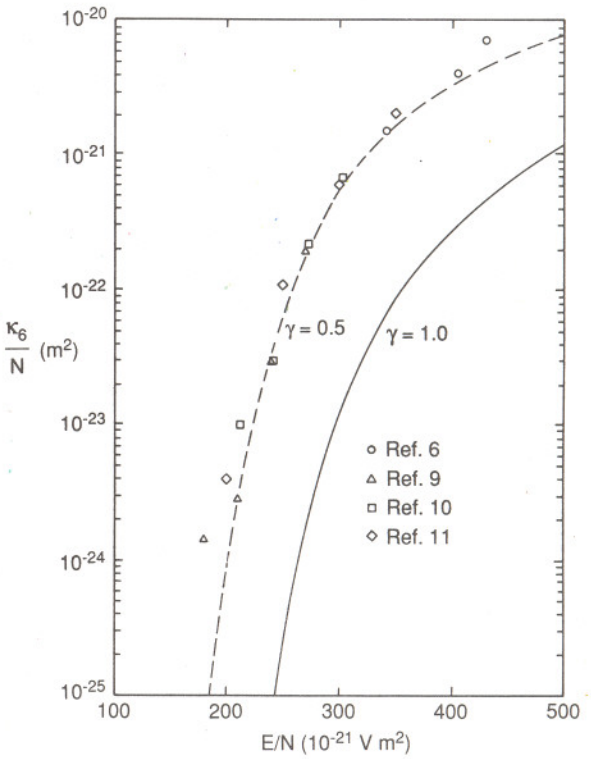

FIG. 4. Calculated reaction coefficients for the reaction $SF_6^- + SF_6 \rightarrow SF_5^- + F + SF_6$ using measured cross-section data $\sigma_6(\epsilon_L)$ and a Kagan and Perel energy distribution. The symbols are previously calculated reaction coefficients for the same process derived from uniform-field drift-tube data.

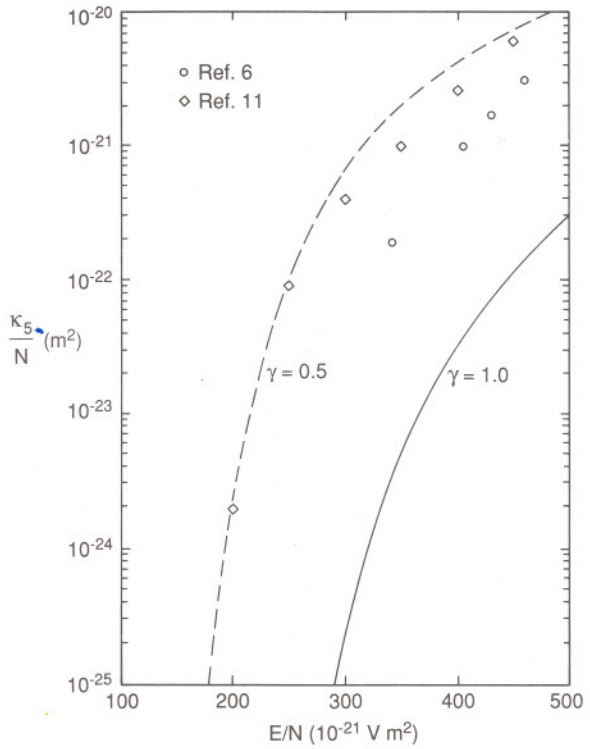

FIG. 5. Calculated reaction coefficients for the reaction $SF_5^- + SF_6 \rightarrow F^- + SF_4 + SF_6$ using measured cross-section data $\sigma_5(\epsilon_L)$ and a Kagan and Perel energy distribution. The symbols are previously calculated reaction coefficients for the same process derived from uniform-field drift-tube data.

The Kagan and Perel distribution in Eq. (5) can be conveniently altered by allowing γ to vary between 0 and 1. The dashed lines in Figs. 4 to 6 represent reaction coefficients calculated with $\gamma = 0.5$, while in Fig. 2 the relative magnitudes of the two distributions ($\gamma = 1$ and $\gamma = 0.5$) are shown for comparison.

Obviously, the curves in Figs. 4, 5, and 6 with $\gamma = 0.5$ are in better agreement with the previously reported coefficients than are the curves calculated using $\gamma = 1$. This may indicate that previously assumed energy distributions need to be modified.[1,7] However, one must note that the reaction coefficients derived from drift-tube data are model dependent and that only reactions 5, 6, and 9 (Table I) are assumed in the previous analysis of data from drift tubes. Thus discrepancies may also arise because this commonly used model does not consider the collision-induced dissociation of SF_6^- into $F^- + SF_5$ (reaction 4, Table I). This reaction is found here to be significant (see Fig. 2) and its omission may produce errors in the reaction rates derived from drift-tube data.

The calculated reaction coefficients for reaction 4 (Table I) (and for reactions 7 and 8, Table I) are shown in Fig. 7 using Kagan and Perel distributions with $\gamma = 1.0$ and 0.5. As stated before, no previously determined coefficients for these processes exist for comparison.

V. A MODEL FOR ELECTRON DETACHMENT DURING ION DRIFT IN SF_6

A different interpretation of the processes which lead to detachment coefficients derived from drift-tube data[6,7] and

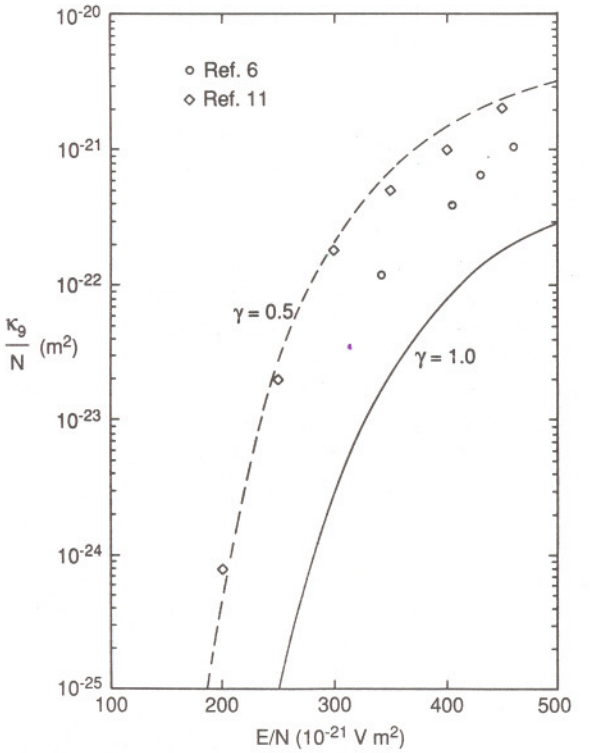

FIG. 6. Calculated reaction coefficients for the reaction $F^- + SF_6 \rightarrow F + SF_6^-$ (see Ref. 16) using measured cross-section data $\sigma_9(\epsilon_L)$ and a Kagan and Perel ion kinetic-energy distribution. The symbols are previously calculated reaction coefficients for the same process derived from uniform-field drift-tube data.

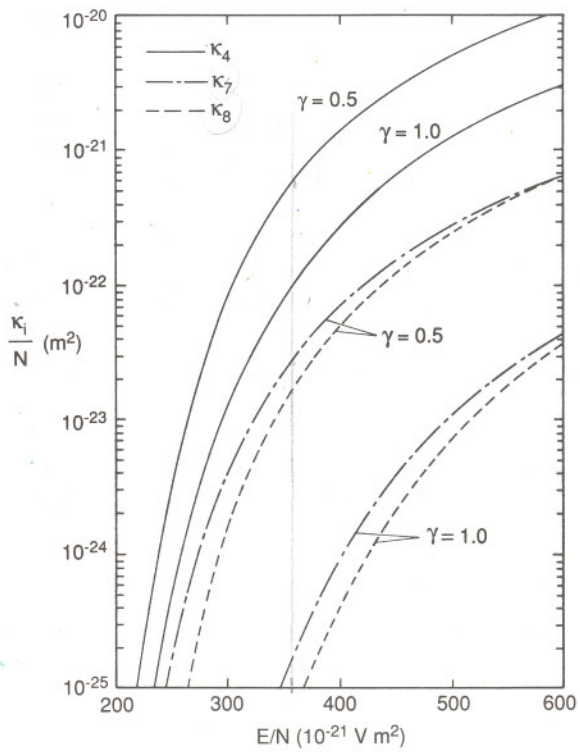

FIG. 7. Calculated reaction coefficients using a Kagan and Perel ion kinetic-energy distribution for the following reactions: (—) $SF_6^- + SF_6 \rightarrow F^- + SF_5 + SF_6$; (–·–) $SF_6^- + SF_6 \rightarrow$ charge-transfer products; and (- - -) $SF_5^- + SF_6 \rightarrow$ charge-transfer products.

their observed pressure dependence can be obtained if one assumes that electron production in a drift tube is not due primarily to prompt electron detachment from SF_6^-, but arises from either detachment from F^- or from collisionally excited, energetically unstable $(SF_6^-)^*$ ions.[35] While the precise role of autodetachment of $(SF_6^-)^*$ cannot be inferred directly from the present measurements, the existence of excited SF_6^- has been previously established.[36,37]

It is assumed, for this model, that under drift-tube conditions, prompt detachment from SF_5^- and SF_6^- is insignificant, and that a steady state condition exists for intermediate products[38] (i.e., $d[SF_5^-]/dt = d[F^-]/dt = d[(SF_6^-)^*]/dt = 0$). If one analyzes the drift-tube data as done previously,[6,7] assuming that all ejected electrons come from SF_6^- ions, then the measured electron-production rate can be written in terms of an "effective" detachment coefficient (δ_{eff}) according to the expression

$$\frac{d[e]}{dt} = v_d \left(\frac{\delta_{\text{eff}}}{N}\right) N[SF_6^-], \tag{10}$$

where $[e]$ is the number of free electrons produced per unit volume which can be detected, v_d refers specifically to the drift velocity of SF_6^- in SF_6, and δ_{eff}/N is determined by analysis of drift-tube data.[6,7] Assuming that the simplified set of processes indicated in Table II dominate in a drift tube, an expression for δ_{eff}/N can be found in terms of the relevant rate coefficients by solving the set of coupled rate equations.[39] The result is

$$k_{\text{eff}} = v_d \left(\frac{\delta_{\text{eff}}}{N}\right) = k_3 \left(\frac{k_6 + k_4}{k_9 + k_3}\right) + k_{12} \left(\frac{k_{10}}{k_{12} + k_{11}N}\right). \tag{11}$$

It should be noted that the process of electron attachment has been neglected in this model because the measurements with which it is to be compared[6,7] were performed at electric-field strengths above the critical value where the ionization rate in SF_6 exceeds the attachment rate. Under these conditions an electron released by detachment has a mean energy high enough that it is much more likely to induce ionization than to reattach.[12] The analysis of the data from drift-tube experiments[6,7] in fact takes into account the amplification effect of the resulting electron current due to ionization.

The effective detachment coefficient given by Eq. (11) is seen to consist of two terms, a pressure-independent term which depends upon various ion conversion and direct-detachment processes involving F^-, and a pressure-dependent term which depends upon the rates for collisional relaxation, excitation, and autodetachment of $(SF_6^-)^*$. This expression is more complex than those previously derived[1,6,7] which assume that direct detachment from SF_6^- was the sole source of electrons.

If $k_{11}N$ is approximately the collision frequency of SF_6^- in SF_6 (e.g., $\sim 10^8$/s at 1 kPa) and k_{12} is on the order of the inverse of the excited-state lifetime ($\tau \sim 10$ μs to 2 ms),[36] then $k_{11}N \gg k_{12}$ and the model predicts an inverse pressure dependence for δ_{eff}/N at low N. This inverse pressure dependence is consistent with previous drift-tube measurements.[6,7] However, the entire set of data from Refs. 6 and 7 cannot be fit to the $A + B/N$ form of Eq. (11), perhaps indicating an inconsistency between the two data sets. O'Neill and Craggs[6] also report no detachment from F^- or SF_5^- at low pressures in agreement with the dominance of the second term of Eq. (11) for smaller N. The model proposed here is consistent with the observed[7] variations in δ_{eff}/N with the "age" of the SF_6^- ions if there is a substantial fraction of SF_6 anions which are initially in excited or autodetaching states.

At higher pressures, the first term on the right-hand side of Eq. (11) dominates, giving a δ_{eff}/N that is essentially pressure independent. In this pressure regime, electron production involves mainly process (3) with a threshold of 8 eV. These results are consistent with (1) the lack of pressure dependence[1,13] for δ_{eff}/N suggested from the analysis of high-pressure electrical discharge initiation data, and (2) previously discussed results[32] suggesting detachment in SF_6 is predominately from F^-.

Ideally, one would like to calculate the effective detachment coefficients using Eq. (11) to compare with the previously determined drift-tube measurements. However, values for k_{10}, k_{11}, and k_{12} are not available, so only the contribution to δ_{eff}/N from the first term of Eq. (11) can be calculated using the reaction coefficients derived above. The solid curve in Fig. 8 shows the contribution from the first term of Eq. (11) using a Kagan and Perel distribution with $\gamma = 1.0$. Note that the magnitude of the solid curve is similar to that of the effective detachment coefficient derived from discharge-inception experiments[2] (dot–dashed curve) but is substantially smaller than the coefficients derived from drift-tube experiments[6,7] (symbols). If one uses the reaction coefficients derived using a Kagan and Perel energy distribution with $\gamma = 0.5$ (dashed curve) then the δ_{eff}/N derived from the first term of Eq. (11) becomes of the same order of magnitude as the coefficients derived from the highest pressure drift-tube experiments. The fact that the dashed curve actually lies above the smallest measured drift-tube values indicates that taking $\gamma = 0.5$ may overestimate the high-energy tail for the kinetic-energy distribution.

It is also important to note that the above model gives a reasonable pressure dependence for δ_{eff}/N without invoking "stabilization" of SF_6^- via (SF_6) SF_6^- dimer formation as proposed by Hansen *et al.*[7] Dimer formation is irrelevant here because: (1) it was introduced to compete with the di-

TABLE II. Proposed ion–molecule reactions for drift tubes containing SF_6.

Reaction	Rate coefficient	
$SF_6^- + SF_6 \rightarrow SF_5^- + F + SF_6$	k_6	dissociative ion conversion
$SF_6^- + SF_6 \rightarrow F^- + SF_5 + SF_6$	k_4	dissociative ion conversion
$SF_5^- + SF_6 \rightarrow F^- + SF_4 + SF_6$	k_5	dissociative ion conversion
$F^- + SF_6 \rightarrow F + SF_6^-$	k_9	charge transfer
$F^- + SF_6 \rightarrow$ neutrals $+ e^-$	k_3	e^- detachment
$SF_6^- + SF_6 \rightarrow (SF_6^-)^* + SF_6$	k_{10}	excitation
$(SF_6^-)^* + SF_6 \rightarrow SF_6^- + SF_6$	k_{11}	deexcitation
$(SF_6^-)^* \rightarrow SF_6 + e^-$	k_{12}	autodetachment

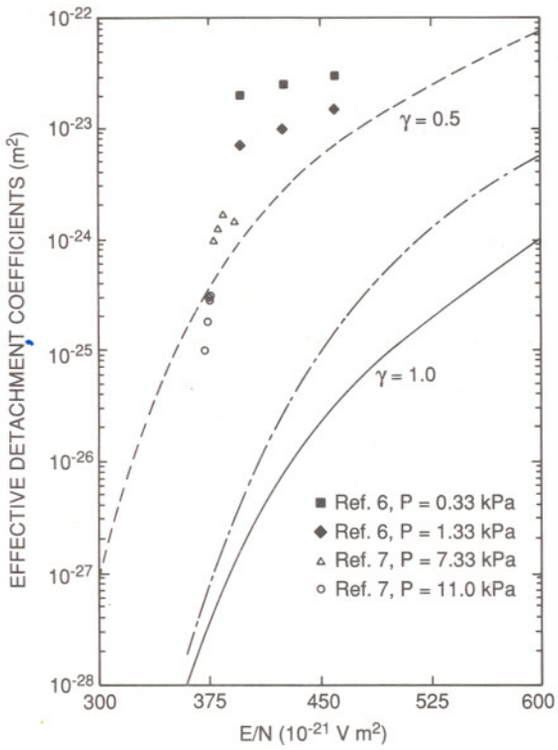

FIG. 8. Effective detachment coefficients determined from drift-tube experiments at different pressures are shown as identified by the symbols in the key. Effective detachment coefficients calculated from discharge-inception data from Ref. 1 are also shown (–·–). The contribution to the effective detachment coefficients from the first term of Eq. (11) are shown for $\gamma = 1.0$ (—) and for $\gamma = 0.5$ (- - -).

rect SF_6^- collisional-detachment process, which is of doubtful significance and (2) it cannot, as can be shown, yield the observed pressure dependence. There are also data which suggest that $(SF_6)SF_6^-$ formation is very slow[30] and decreases with increasing E/N.[40]

IV. CONCLUSIONS

Calculations of the electron-detachment coefficients from the measured cross sections presented in a companion paper[14] which exhibit high energetic thresholds are compatible with the hypothesis that prompt electron detachment from either SF_6^- or SF_5^- in SF_6 is insignificant under the experimental operating conditions of previous drift-tube and discharge-inception experiments.

Reaction coefficients calculated for ion-conversion processes which also use the measured cross sections[14] indicate the necessity to reexamine both ion-conversion coefficients determined in SF_6 from drift-tube data and the ion kinetic-energy distributions assumed in interpreting the results of those experiments. Some of the discrepancies between the ion-conversion reaction coefficients predicted here and those determined from analysis of drift-tube data may be explained by the absence of the reaction $SF_6^- + SF_6 \rightarrow F^- + SF_5 + SF_6$ from the model used to analyze drift-tube data. This process has been shown to be significant. However, it is doubtful that the omission of this reaction is the sole cause of the large discrepancies (up to several orders of magnitude) displayed in Figs. 4–6 between experimental results and calculations using a Kagan and Perel distribution. Therefore, it is suspected that the standard forms for the kinetic-energy distribution often assumed[1,7] for ions in SF_6 are not appropriate and that the actual kinetic-energy distributions for all negative ions have substantially larger high-energy tails than implied, for example, by either the Kagan and Perel or Maxwellian distributions.

The measured cross sections have been used in a theoretical model which invokes detachment from long-lived, energetically unstable states of collisionally excited SF_6^- to explain the pressure dependence of previously measured detachment coefficients and the high apparent detachment thresholds implied by analysis of breakdown-probability data for SF_6. The model suggests that measured effective detachment coefficients depend upon many different reaction rates, thus implying that detachment processes in SF_6 are more complex than previously assumed. At high pressures, measured detachment coefficients appear to depend primarily upon the rates for ion-conversion and direct-detachment processes involving F^-, consistent with earlier suggestions.

ACKNOWLEDGMENTS

This research was supported, in part, by the U. S. Department of Energy Office of Basic Energy Sciences, Division of Chemical Science (W & M) and Office of Electric Energy Systems (NIST).

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