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EFFECT OF TEMPERATURE ON THE ELECTRON ATTACHMENT AND DETACHMENT PROPERTIES OF c-C_4F_6

P. G. Datskos#, L. G. Christophorou#, and J. G. Carter

Atomic, Molecular, and High Voltage Physics Group,
Health Sciences Research Division,
Oak Ridge National Laboratory,
Oak Ridge, Tennessee 37831-6122, U.S.A.

ABSTRACT

The temperature dependence of the low-energy electron attachment and autodetachment processes for c-C_4F_6 in a N_2 buffer gas has been studied in the temperature, T, range of 300 to 600 K and the mean electron energy, $<\varepsilon>$, range from 0.19 to 1.0 eV. The low-energy electron attachment rate constant for c-C_4F_6 shows only a slight dependence on gas temperature. In contrast, the autodetachment frequency increases by more than four orders of magnitude when T is increased from 300 to 600 K. This increase in autodetachment is due to the increase in the internal energy content of the c-$C_4F_6^-$ anion with increasing T. The autodetachment process under consideration is a heat-activated process and has an activation energy E^* of 0.24 eV. The significance of these results to gaseous dielectrics is indicated.

INTRODUCTION

The electron attachment and detachment properties of dielectric gas molecules play an important role in determining their dielectric properties[1-3]. For example, at room temperature the large electron attachment cross sections[4] for hexafluorobutene (c-C_4F_6), hexafluorobenzene (C_6F_6) and sulfur hexafluoride (SF_6) which at low electron energies are due to both parent and fragment anions are primarily responsible for their high dielectric strengths[2,3]. As high electron attachment leads to high dielectric strength, the presence of

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#Also at The Department of Physics and Astronomy, The University of Tennessee, Knoxville, Tennessee 37996-1200.

electron detachment can lead to the production of avalanche initiating electrons[5-7] and high probability of detachment can result in a reduction of the dielectric strength of a gaseous medium (e. g., see Ref. 8 and later in this paper).

Changes in the internal energy of a molecule can drastically affect its electron attaching and detaching properties. Such changes in the internal energy content of a molecule can be effected by gas heating or by laser irradiation. Modifying the ability of an electronegative gas to capture and to release electrons results in alteration of its dielectric properties. For example, the decline in the limiting electric field strength, $(E/N)_{lim}$, with increasing T reported earlier[8] for dielectric gases which at low electron energies form parent anions can be attributed to increased autodetachment, while the increase in $(E/N)_{lim}$ for gases which capture electrons only dissociatively, can be attributed to the increase in the negative ion formation due to enhancement of dissociative electron attachment with increasing T[8].

In this paper we report on the effect of temperature, T, on the electron attachment rate constant, $k_a(<\varepsilon>,T)$, and the electron detachment frequency, $t_d^{-1}(T)$ for c-C_4F_6 and c-$C_4F_6^-$, respectively, in a buffer gas of N_2 for electron energies ≤ 1 eV. In this electron energy range c-C_4F_6 captures electrons nondissociatively, very efficiently[9], forming long-lived ($\tau_a > 6\mu s$[10]) parent negative ions. At energies above 2 eV fragment anions (F^-, $C_3F_3^-$, and $C_4F_5^-$) are produced with much lower cross sections[10].

The electron attachment and detachment processes envisioned are

$$e + c\text{-}C_4F_6 \xrightarrow{k_c} c\text{-}C_4F_6^{-*} + (N_2) \xrightarrow{p} c\text{-}C_4F_6^- \qquad (1)$$

$$c\text{-}C_4F_6^- \xrightarrow{t_d^{-1}} c\text{-}C_4F_6 + e \qquad (2)$$

namely, electrons are captured by c-C_4F_6 molecules with a rate constant $k_c(T)$ forming transient c-$C_4F_6^{-*}$ anions which then are stabilized via collisions with, primarily, the buffer gas (N_2) molecules with a probability of stabilization per colission *p* yielding stable c-$C_4F_6^-$ anions. The captured electrons can then thermally autodetach from the stable anion [reaction (2)] with a detachment frequency t_d^{-1}.

EXPERIMENTAL TECHNIQUE

In Fig. 1 is shown a schematic of the experimental arrangement employed. The cell consisted of a six-way stainless-steel cube with one sapphire window and two electrical feedthroughs. The two parallel stainless steel electrodes were held at a distance of ~0.42 cm. The electron swarm was produced by a fast N_2 laser pulse (FWHM ~6×10^{-10} s) which strikes the cathode through a 0.1 cm-diameter hole in the anode electrode.

The cell was filled with small quantities of electron attaching gas c-C_4F_6 in a buffer gas of N_2. The N_2 gas number density, N_T, was varied from 1.61×10^{19} to 9.66×10^{19} molecules cm^{-3} and the attaching gas number density N_a was varied from 1.6×10^{13} to 64.4×10^{13} molecules cm^{-3}. Under the influence of an applied uniform electric field the electron swarm drifts towards the anode . The electron energy distribution $f(\varepsilon,E/N,T)$ is characteristic of N_2 since $N_a \ll N_T$. As the electrons drift a fraction of them is captured by the c-C_4F_6 molecules via reaction (1). Heat-activated detachment [reaction (2)] gives rise to delayed electrons which can be in the drift gap long after the initial (prompt) electrons have reached the anode. The induced electron current monitored as a function

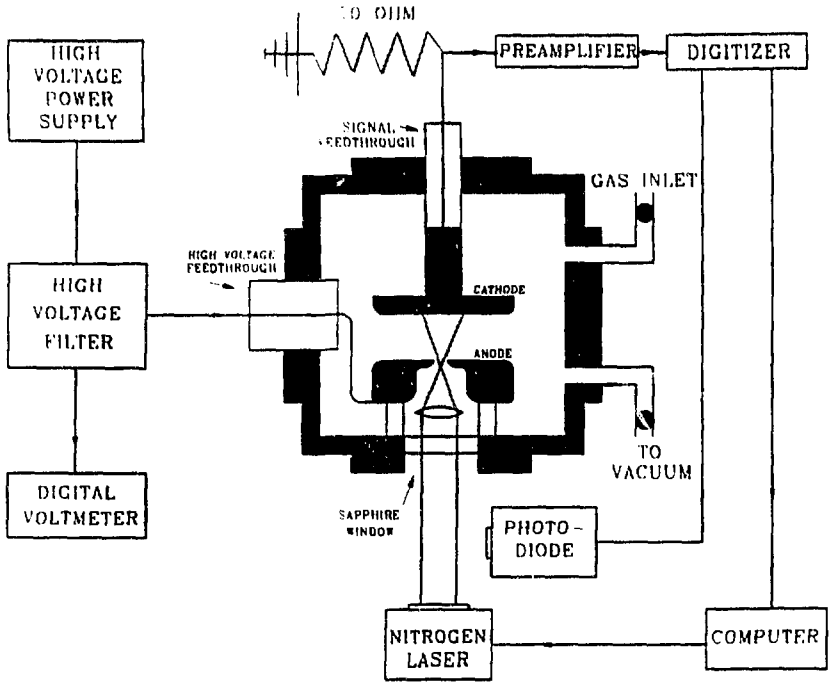

Figure 1. Schematic diagram of the experimental apparatus used in the present studies.

of time can be described by[11,12]

$$i_e(t) = \frac{e w_e}{d} \int_{w_i t}^{\min[w_e t,\, d]} \rho_e(x,t)\, dx \tag{3}$$

where $\rho_e(x,t)$ is the electron number density; w_e and w_i are the electron and ion drift velocities ($w_e \gg w_i$) and d is the drift distance. When the initial electrons are produced by a short duration laser pulse, *i.e.*, for initial conditions $\rho_e(x,0)=n_0\delta(x)$ the electron number density is given by[11-15]

$$\rho_e(x,t) = \frac{n_0}{w_e - w_i} \exp\left[-\frac{1}{t_a}\left(\frac{x - w_i t}{w_e - w_i}\right) - \frac{1}{t_d}\left(\frac{w_e t - x}{w_e - w_i}\right)\right] \times \left[\delta\left(\frac{w_e t - x}{w_e - w_i}\right) + \sqrt{\frac{1}{t_a t_d}\frac{x - w_i t}{w_e t - x}} \times I_1\left(\frac{2}{(w_e - w_i)}\sqrt{\frac{1}{t_a t_d}(w_e t - x)(x - w_i t)}\right)\right] \tag{4}$$

where t_a^{-1} and t_d^{-1} are, respectively, the electron attachment and detachment frequencies, n_0 is the initial number of electrons in the swarm (i.e. the number of electrons at $x=0$, $t=0$), and I_1 is the first order modified Bessel function.

The change in the electron current due to the removal (electron attachment) and gain (autodetachment) of electrons as T is increased and thus as the internal energy content of the neutral molecules and anions is increased can be viewed in the typical experimental waveforms shown in Fig. 2. The evolution of the autodetachment process and its effect on the electron current as T is increased is clearly seen for this gas in Fig. 2.

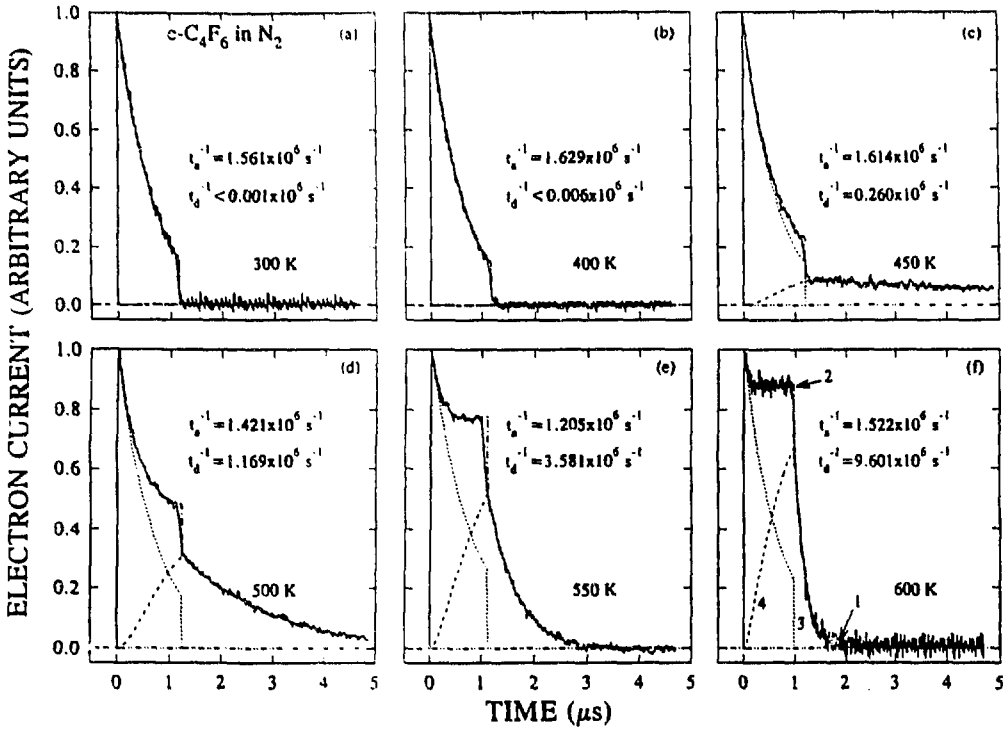

Figure 2. Electron current waveforms for c-C_4F_6 in N_2 at T=300, 400, 450, 500, 550, and 600 K. All waveforms are for E/N=1.24x10^{-17} V cm^2, N_T=6.44x10^{19} molecules cm^{-3}, N_a=6.44x10^{13} molecules cm^{-3}. The solid curves (—; curve 1 in Fig. 2f) are the experimentally measured total electron currents as a function of time; the dash-dot (-·-·-) curves (curve 2; Fig. 2f) are the calculated electron current waveforms for the t_a^{-1} and t_d^{-1} values obtained from the fitting of Eqn (3) (see the text and the values of t_a^{-1} and t_d^{-1} given in the figure) to curves 1; the dotted (···) curves (curve 3; Fig. 2f) represent the contribution to the electron current of the initial (prompt) electron swarm when only electron attachment occurs, and the broken (– –) curves (curve 4; Fig. 2f) represent the contribution to the electron current from the autodetached electrons.

RESULTS AND DISCUSSION

Electron Attachment Rate Constant $k_a(<\varepsilon>,T)$

From waveforms such as those in Fig. 2 we determined the $t_a^{-1}(<\varepsilon>,T)$ and $t_d^{-1}(<\varepsilon>,T)$ simultaneously via a nonlinear least squares fit procedure to Eqn (3) for a number of mean electron energies and gas temperatures. The rate constant for electron attachment was then determined as $k_a=t_a^{-1}/N_a$ where N_a is the attaching gas number density. The $k_a(<\varepsilon>,T)$ for c-C_4F_6 was found to be independent of N_a at all T studied. A small increase in $k_a(<\varepsilon>,T)$ with increasing N_T was observed indicating a more efficient collisional stabilization of the transient c-$C_4F_6^{-*}$ anion at higher N_T. In order to account for this increase we determined the values of $\lim_{N_T\to\infty}[k_a(<\varepsilon>,T)]$ by plotting the measured $1/k_a$ at each N_T as a function of $1/N_T$ and extrapolating $1/N_T$ to 0, at each T. These values of $k_a(<\varepsilon>,T)$ are plotted in Fig. 3 as a function of $<\varepsilon>$ for a number of temperatures. It can be seen that the effect of T on $k_a(<\varepsilon>,T)$ is small.

Autodetachment Frequency $t_d^{-1}(<\varepsilon>,T)$

The gas temperature has a profound effect on reaction (2) for c-C_4F_6. This is clearly

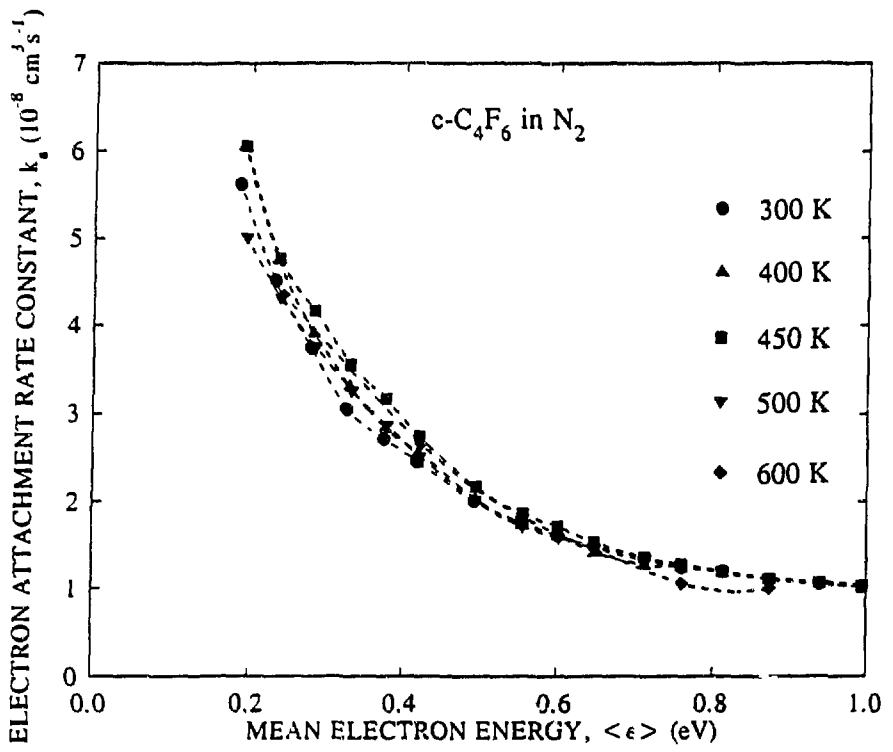

Figure 3: k_a vs. $<\varepsilon>$ for c-C_4F_6 at the indicated temperatures.

shown in Fig. 2 where the measured electron current waveforms change significantly with gas temperature. The t_d^{-1} we determined for c-$C_4F_6^-$ are plotted in Fig. 4 as a function of $<\varepsilon>$ for T= 450, 500, 550, and 600 K. Below 450 K the electron detachment is very small and only an upper limit can be placed on t_d^{-1}; t_d^{-1} is $< 10^3$ s^{-1} at T=300 K and $< 6x10^3$ s^{-1} at T=400 K. For the N_2 gas number densities used, the c-$C_4F_6^{-*}$ anions undergo a large number of collisions within the lifetime of the "isolated" c-$C_4F_6^{-*}$ anions[10,12]. We can then assume that the preponderance of the c-$C_4F_6^-$ ions are in their lowest vibrational/rotational energy state allowed at each T when the electron is thermally detached from them. At each T employed we estimated the vibrational energy, $<\varepsilon>_{int}(T)$ of the c-C_4F_6 molecules in excess of the zero-point energy using the vibrational frequencies of Ref. 16. We then assumed that the total internal energy content for the c-$C_4F_6^-$ anions is the same as for the neutral c-C_4F_6 molecule and plotted (Fig. 5) t_d^{-1} as a function of $<\varepsilon>_{int}$. It can be seen that $t_d^{-1}(<\varepsilon>_{int})$ increases by more than three orders of magnitude as $<\varepsilon>_{int}$ changes from ~0.16 to ~0.56 eV; $t_d^{-1} < 10^3$ s^{-1} at $<\varepsilon>$ ~0.16 eV (see Fig. 2).

Dependence of the Anion Autodetachment on the Molecular Electron Affinity

If we assume that all the c-$C_4F_6^-$ ions are in their lowest vibrational/rotational state allowed at each T and that when they autodetach they reach the same energy state for the neutral molecule, then t_d^{-1} may be related to T by

$$t_d^{-1} = t_{d0}^{-1} e^{-E^*/kT} \qquad (5)$$

where E^* is the activation energy of process (2) and t_{d0}^{-1} is the autodetachment frequency when $T \rightarrow \infty$. When our measured autodetachment frequencies are plotted as $\ln(t_d^{-1})$ vs. $1/T$ a straight line is obtained (Fig. 6) from which we estimated E^* to be 0.237 eV. A similar

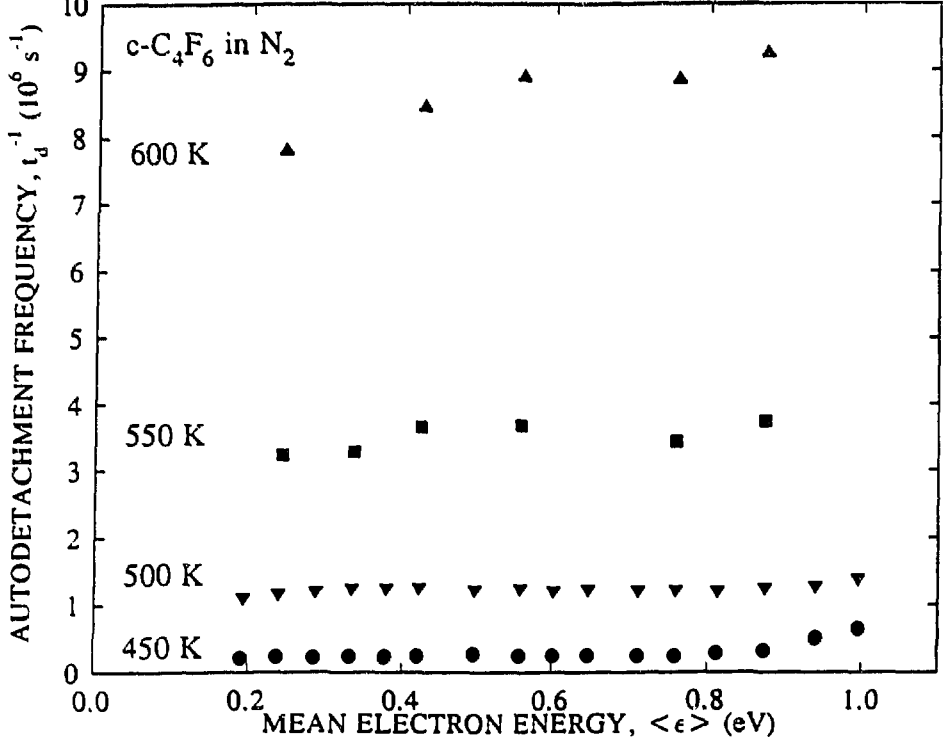

Figure 4: $t_d^{-1}(<\epsilon>,T)$ vs. $<\epsilon>$ for c-$C_4F_6^-$ at the indicated temperatures.

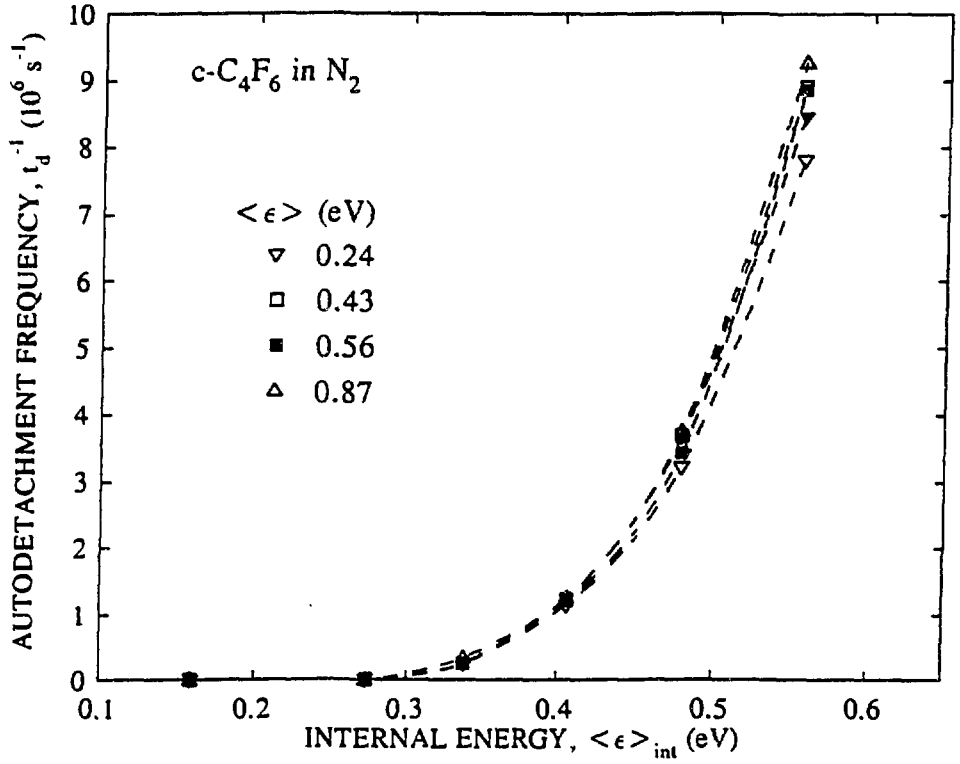

Figure 5: t_d^{-1} vs. $<\epsilon>_{int}$ for c-$C_4F_6^-$ for four values of $<\epsilon>$.

study[11] for $C_6F_6^-$ gave a value for E^* equal to 0.477 eV. If we take E^* to be an estimate of the electron affinity (EA) of the molecule, then $E^*(C_6F_6^-)$ compares well with the reported[17] $EA(C_6F_6)$ of 0.52 eV. There are no reported values for the $EA(c\text{-}C_4F_6)$ but we can take $E^*(c\text{-}C_4F_6^-)$=0.24 eV to be a lower estimate. The large electron detachment can then be understood on the basis of the small values of EA for these molecules since the smaller the E^* the larger the exponential term in Eqn (5). Consistent with this, for SF_6 for which the EA is 1.05 eV[18] we observed[13] no electron detachment from SF_6^- below 600 K.

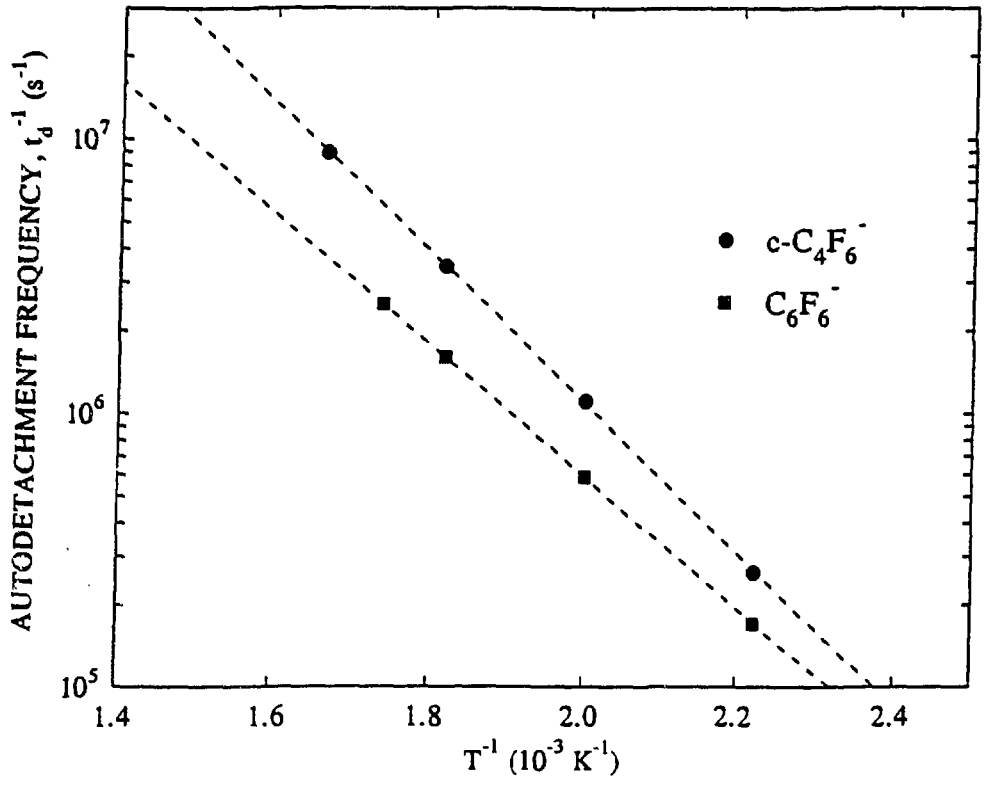

Figure 6: t_d^{-1} vs. 1/T for c-$C_4F_6^-$ and $C_6F_6^-$.

Dependence of the Dielectric Strength on Electron Attachment and Detachment

Earlier studies[8] have shown that the $(E/N)_{lim}$ for electronegative gases which at low electron energies form parent negative ions decreases with increasing gas temperature and for molecules that capture electrons only dissociatively the $(E/N)_{lim}$ increases with increasing T. For example, the $(E/N)_{lim}$ for c-C_4F_8 declined by as much as 20% as T was raised from 297 to 573 K and the $(E/N)_{lim}$ for $CClF_3$ increased by ~ 3% in the T-range 294 to 573 K[8]. A similar but larger increase in $(E/N)_{lim}$ (~14%) was recently observed[12] for SF_6 which at low electron energies forms predominantly parent negative ions and at higher energies only fragment negative ions. The decrease in $(E/N)_{lim}$ with increasing T is related to increases in the heat-activated electron detachment which is likely for dielectric gases which capture electrons forming parent anions while the increase in the dielectric strength with increasing gas temperature follows the T-dependence of the dissociative electron attachment.

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