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CALCULATION OF ELECTRIC FIELD-INDUCED DETACHMENT RATE OF ELECTRONS FROM MONONEGATIVE IONS; RELEVANCE TO GASEOUS DIELECTRICS*

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ABSTRACT

Our model for the mononegative atomic or molecular ion in its effect on the most loosely bound electron is a "spherical square well" (constant positive inner potential within a sphere of radius r_0 and zero potential outside). From it we have calculated by quantum mechanics the emission rate $w_{\nu\ell m}$ of electrons from the ν^{th} excited state (of orbital angular momentum and magnetic quantum numbers ℓ and m and energy $E_{\nu\ell} < 0$) under the influence of a constant electric field F . The calculation is conceptionally simple (involving time-dependent perturbation theory) but technically complicated (requiring an eleven-fold integration), and leads to a surprisingly simple final expression. The relevance of our calculations to gaseous dielectrics is discussed.

INTRODUCTION

We have repeatedly pointed out earlier (e.g., see Ref. 1) that the most desirable way of removing electrons from an electrically stressed gaseous dielectric--in order to effect a higher dielectric strength--is capture of the electrons by the dielectric gas molecules forming negative ions. These ions diffuse to the walls of the container and are destroyed there. If, however, the electrons are loosely bound to the atom, radical, or molecule (i.e., if the electron affinity, EA, of the capturing species is small, say, close to $3/2$ kT), the ions, A^- , can be efficiently destroyed in collisions with neutral species (via the processes of associative and nonassociative collisional detachment) and/or by electric fields (field-induced electron detachment) when the latter are large. It is of course possible that other electron detachment processes (e.g., photodetachment, electron impact-induced detachment; see Chap. 7 of Ref. 2 and Discussion) can occur. A host of observations in breakdown studies have been attributed to electric field-induced electron detachment from negative ions. Very little, however, is known about this process and its implied role in breakdown phenomena. Some work has been reported

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earlier in connection with particle accelerators. For example, the field-induced detachment from the simple atomic negative ions He^- ($1s2s2p$), H^- ($1s^2$), and D^- ($1s^2$) has been studied (Refs. 3-5, 4-8 and 9, respectively). Constant uniform electric fields of the order of 100 kV/cm and 2 MV/cm were found to be necessary to detach electrons from He^- and H^- , respectively. The binding energy of the electron in He^- ($1s2s2p$) and H^- ($1s^2$) is 0.075 and 0.75 eV, respectively (Ref. 2, Chap. 7).

In this paper we estimate the transition probability per unit time of an electron from a singly charged atomic or molecular negative ion to the continuum under the influence of a static electric field as a function of the angular momentum quantum number, l , the magnetic quantum number, m , the EA, and the size of the anion. We also discuss the implications of the obtained results to gaseous dielectrics.

ELECTRIC FIELD-INDUCED DETACHMENT OF AN ELECTRON FROM A MONONEGATIVE ION

In this section a calculation is presented of the transition probability per unit time of an electron from a singly charged atomic or molecular negative ion to the continuum under the influence of a static electric field. We choose singly charged ions to insure that the interaction between electron and residual atom or molecule at large separations is weaker than the Coulomb interaction. We assume that the applied electric field is uniform and weak compared to the atomic field.* The transition probability per unit time is, then, small compared to the atomic unit of transition probability per unit time. These assumptions imply that the electron becomes free by tunneling through a potential barrier of appreciable size.

The wave function ψ_{olm} of the most weakly bound electron is assumed to feel no force for $r \geq r_0$, where r_0 is the radius of a sphere which contains all save a small fraction f_0 of this most weakly bound electron's charge. The energy of this electron is negative, equal to $E_{ol} = -(EA)$. The wave function for $r > r_0$ then satisfies $-(\hbar^2/2m)\nabla^2 \psi_{olm} = E_{ol} \psi_{olm}$, where ∇^2 is Laplace's operator. We shall also write $-(EA) = -\hbar^2 \kappa^2/2m$ to get the simplified equation $\nabla^2 \psi_{olm} = \kappa^2 \psi_{olm}$ for the outer part of the wave function. We shall need none of the details of the wave function or potential energy for $r < r_0$ except that the energy is $-(EA)$ and that the solutions have the transformation properties of the spherical harmonics $Y_{lm}(\theta, \phi)$ and are properly continuous with continuous radial derivative at $r = r_0$.

Solutions to the scalar Helmholtz equation with imaginary wave vector are well-known. Choosing those which vanish exponentially as $r \rightarrow \infty$, we have

$$\psi_{olm}(r, \theta, \phi) = c_{ol} h_l^{(1)}(i\kappa r) Y_{lm}(\theta, \phi),$$

*In the following, $-e$ and m are the charge and mass of the electron, $\hbar = h/2\pi$ (where h is Planck's constant), and c is the speed of light. The unit of length is the radius of the first Bohr orbit, $a_H = \hbar^2/me^2 \approx 0.53 \times 10^{-8}$ cm; the unit of energy is the Rydberg, $e^2/2a_H \approx 13.6$ eV; the unit of electric field is the atomic field, $e/a_H^2 \approx 5 \times 10^9$ volt cm^{-1} ; and the unit of transition probability is $(e^2/2a_H)/\hbar \approx 2 \times 10^{16}$ sec^{-1} .

where $h_\ell^{(1)}$ is the spherical Hankel function of the first kind. Our normalization condition becomes

$$\int_{r_0}^{\infty} |c_{o\ell} h_\ell^{(1)}(ikr)|^2 r^2 dr = f_\ell.$$

We shall write

$$c_{o\ell} = i^{\ell+2} (\kappa^3 f_\ell)^{1/2} / N_\ell(\kappa r_0)$$

because $i^{\ell+2} h_\ell^{(1)}(ikr)$ is a real positive function of the real positive variable κr ; here

$$N_\ell(x) = \left\{ \int_x^\infty |h_\ell^{(1)}(ix)|^2 x^2 dx \right\}^{1/2}.$$

For $0 \leq \ell \leq 4$, $i^{\ell+2} h_\ell^{(1)}(ix)$ and $[N_\ell(x)]^2$ are given in Table 1.

TABLE 1 Values of $i^{\ell+2} h_\ell^{(1)}(ix)$ and $[N_\ell(x)]^2$ for $0 \leq \ell \leq 4$

ℓ	$i^{\ell+2} h_\ell^{(1)}(ix)$	$[N_\ell(x)]^2$
0	$x^{-1} e^{-x}$	$e^{-2x} (1/2)$
1	$x^{-1} e^{-x} (1+x^{-1})$	$e^{-2x} (1/2 + 1/x)$
2	$x^{-1} e^{-x} (1+3x^{-1}+3x^{-2})$	$e^{-2x} (1/2 + 3/x + 6/x^2 + 3/x^3)$
3	$x^{-1} e^{-x} (1+6x^{-1}+15x^{-2}+15x^{-3})$	$e^{-2x} (1/2 + 6/x + 30/x^2 + 75/x^3 + 90/x^4 + 45/x^5)$
4	$x^{-1} e^{-x} (1+10x^{-1}+45x^{-2}+105x^{-3}+105x^{-4})$	$e^{-2x} (1/2 + 10/x + 90/x^2 + 465/x^3 + 1470/x^4 + 2835/x^5 + 3150/x^6 + 1575/x^7)$

In the presence of an electric field E whose only component is $E_z < 0$, the force on the electron is $-eE_z = F > 0$ and the potential energy of the electron is $-Fz$. In the region $r > r_0$ the Schrödinger equation for the wave function $\psi_{k_x k_y E}(xyz)$ of the electron in the field is

$$-(\hbar^2/2m)\nabla^2\psi - Fz\psi = E\psi.$$

The solutions to this equation are sinusoidal in the x and y directions and Airy functions of z . For the former dependence we first quantize k_x to $2\pi n_1/L_1$ and k_y to $2\pi n_2/L_2$, where n_1 and n_2 are integers, leading to $(L_1 L_2)^{-1/2} \exp i(k_x x + k_y y)$ for this part of ψ ; later we shall replace the sum over discrete k_x and k_y by infinite integrations over k_x and k_y , which requires an extra factor $L_1 L_2 / (2\pi)^2$. For the Airy function we take (Ref. 10)

$$Ai(\zeta) = (2\pi)^{-1} \int_{-\infty}^{\infty} \exp i(w\zeta + w^3/3) dw.$$

After some manipulation our continuum wave function takes the form

$$\psi_{k_x k_y E}(xyz) = (L_1 L_2 F)^{-1/2} (2\pi)^{-1} \int_{-\infty}^{\infty} \exp(i\mathbf{k} \cdot \mathbf{r}) \exp(-ik_z^3/3B^3) \exp(ik_z \epsilon/F) dk_z$$

where $B^3 = 2mF/\hbar^2$ and $\epsilon = E - \hbar^2(k_x^2 + k_y^2)/2m$. The normalization of this wave function (with respect to infinite spatial integration) is

$$(\psi_{k_x k_y E}, \psi_{k_x^1 k_y^1 E^1}) = (4\pi^2/L_1 L_2) \delta(k_x - k_x^1) \delta(k_y - k_y^1) \delta(E - E^1).$$

To obtain the transition probability per unit time $w_{\ell m}$ from the localized state $\psi_{o\ell m}$ to the continuum, we enter the time-dependent Schrödinger equation $H\Psi = i\hbar\partial\Psi/\partial t$ with the time-dependent wave function

$$\Psi(x,y,z,t) = c_{o\ell m}(t) \psi_{o\ell m} \exp(-iE_{o\ell}t/\hbar) + \iiint_{-\infty}^{\infty} c(k_x k_y E, t) \psi_{k_x k_y E} \exp(-iEt/\hbar) (L_1 L_2/4\pi^2) dk_x dk_y dE,$$

subject to the initial conditions $c_{o\ell m}(0) = 1$, $c(k_x k_y E, 0) = 0$. We find that the probability $p_{\ell m}(t)$ of being in any state of the continuum at time $t > 0$ is

$$p_{\ell m}(t) = \iiint |c(k_x k_y E, t)|^2 (L_1 L_2/4\pi^2) dk_x dk_y dE.$$

We also find that the coefficients $c(k_x k_y E, t)$ are given by

$$c(k_x k_y E, t) = \langle k_x k_y E | Fz | o\ell m \rangle \left\{ [(\exp i(E - E_{o\ell})t/\hbar - 1)/(E - E_{o\ell})] \right\}.$$

The absolute square of the term in braces acts, with respect to our energy integration, like $(2\pi\hbar) \delta(E - E_{o\ell})$. After our energy integration, the probability of the electron being in the continuum is

$$p_{\ell m}(t) = (2\pi\hbar) \iint |\langle k_x k_y E_{o\ell} | Fz | o\ell m \rangle|^2 (L_1 L_2/4\pi^2) dk_x dk_y.$$

Three observations are important here. First, since $p_{\ell m}(t)$ is proportional to the time t , we can indeed define a transition probability per unit time $w_{\ell m} = p_{\ell m}(t)/t$ for the electron to go from the localized state $\psi_{o\ell m}$ to any state of the continuum. Second, we are unable to evaluate explicitly the matrix element in angular brackets for a general energy E , but we can evaluate it for the special energy $E_{o\ell}$ for which energy is conserved. Third, because no direction perpendicular to the field is preferred, the dependence of the integral on k_x and k_y reduces to a dependence on $k_x^2 + k_y^2$, and the double integration reduces to a single integration.

Electric Field-Induced Detachment from Mononegative Ions

To evaluate the desired matrix element, we use generalizations of the well-known integral $\int r^{-1} \exp(-\kappa r - i\mathbf{k} \cdot \mathbf{r}) d\mathbf{r} = 4\pi/(\kappa^2 + k^2)$, along with its derivative with respect to $-ik_z$ (which introduces a factor z under the integral sign). After some algebraic manipulation, we have

$$\langle k_x k_y E_{0\ell} | Fz | o_{\ell m} \rangle = [i^{\ell+2}/2\pi N_{\ell}(\kappa r_0)] (\kappa^3 F_{\ell} F/L_1 L_2)^{1/2} \times \int_{-\infty}^{\infty} \exp(ik_z^3/3B^3) \exp(-ik_z \epsilon_{0\ell}/F) i\partial I_{\ell m}^{(1)}/\partial k_z dk_z$$

where

$$I_{\ell m}^{(1)}(\kappa, k_x, k_y, k_z) = \iiint \exp(-i\mathbf{k} \cdot \mathbf{r}) h_{\ell}^{(1)}(ikr) Y_{\ell m}(\theta\phi) r^2 dr d\Omega.$$

We note that the operator $i\partial/\partial k_z$ acting on $I_{\ell m}^{(1)}$ introduces an additional factor z into the integrand of $I_{\ell m}^{(1)}$, and that any polynomial operator $P(i\partial/\partial k_x, i\partial/\partial k_y, i\partial/\partial k_z)$ acting on $I_{\ell m}^{(1)}$ produces an additional polynomial factor $P(x, y, z)$ in that integrand.

The integral $I_{\ell m}^{(1)}$ can be evaluated by standard methods: (a) expanding $\exp(-i\mathbf{k} \cdot \mathbf{r})$ and doing the solid angle integration, which introduces a factor $4\pi(-i)^{\ell} j_{\ell}(\kappa r) Y_{\ell m}(\theta_{\mathbf{k}} \phi_{\mathbf{k}})$ in the integrand; (b) subtracting $j_{\ell}(\kappa r)$ times the differential equation satisfied by $h_{\ell}^{(1)}(ikr)$ from $h_{\ell}^{(1)}(ikr)$ times the differential equation satisfied by $j_{\ell}(\kappa r)$, and transforming part of the result by Green's theorem.[†] We thus find that

$$I_{\ell m}^{(1)}(\kappa, k_x, k_y, k_z) = 4\pi(-1)^{\ell+1} k^{\ell} Y_{\ell m}(\theta_{\mathbf{k}} \phi_{\mathbf{k}}) / \kappa^{\ell+1} (\kappa^2 + k^2).$$

The term $k^{\ell} Y_{\ell m}(\theta_{\mathbf{k}} \phi_{\mathbf{k}})$ is a polynomial in k_x, k_y , and k_z which we shall call $H_{\ell m}(\kappa, k_x, k_y, k_z)$. The quotient $H_{\ell m}/(\kappa^2 + k^2)$, with both numerator and denominator considered to be functions of k_z (because a k_z integration is required) is a polynomial $P_{\ell m}(\kappa, k_x, k_y, k_z)$ plus a rational term $Q_{\ell m}(\kappa, k_x, k_y, k_z)/(\kappa^2 + k_x^2 + k_y^2 + k_z^2)$, in which $Q_{\ell m}$ is a polynomial of degree zero or one in k_z . This rational term can safely be integrated by parts. Here the fortunate circumstance referred to earlier helps us in that with $E = E_{0\ell}$, $\epsilon_{0\ell} = E_{0\ell} - \hbar^2(\kappa_x^2 + \kappa_y^2)/2m = -(\hbar^2/2m)(\kappa^2 + k_x^2 + k_y^2)$ [and recalling that $\hbar^2/2mF = B^{-3}$], the differential of the remainder of the integrand introduces a factor $\kappa^2 + k^2$, which exactly cancels the denominator of $Q_{\ell m}$. The result for the desired matrix element is

[†]The integral over all space uses the external form of $\psi_{o_{\ell m}}$ in the internal region $0 < r < r_0$. This is permissible because the Airy function in this region vanishes far more strongly than $h_{\ell}^{(1)}$ diverges, for the field strengths considered here.

$$\langle k_x k_y E_{0\ell} | Fz | 0\ell m \rangle = [i^{\ell+2}/2\pi N_\ell(\kappa r_0)] (\kappa^3 f_\ell F/L_1 L_2)^{1/2} 4\pi(-1)^{\ell+1} x$$

$$\int_{-\infty}^{\infty} \exp(i k_z^3/3B^3) \exp(-i k_z \varepsilon_{0\ell}/F) [B^{-3} Q_{\ell m} + i \partial P_{\ell m} / \partial k_z] dk_z.$$

$P_{\ell m}$ and $Q_{\ell m}$ are given in Table 2 for $0 \leq |m| \leq \ell \leq 4$. For m negative, the relationship $H_{\ell m}^* = (-1)^m H_{\ell, -m}$, which follows from the phase conventions for the spherical harmonics $Y_{\ell m}$, should be used.

TABLE 2. $P_{\ell m}$ and $Q_{\ell m}$

$P_{00} = 0$	$Q_{00} = (1/4\pi)^{1/2}$
$P_{10} = 0$	$Q_{10} = (3/4\pi)^{1/2} k_z$
$P_{11} = 0$	$Q_{11} = -(3/8\pi)^{1/2} (k_x + ik_y)$
$P_{20} = (5/4\pi)^{1/2}$	$Q_{20} = -(5/4\pi)^{1/2} [\kappa^2 + (3/2)(k_x^2 + k_y^2)]$
$P_{21} = 0$	$Q_{21} = -(15/8\pi)^{1/2} (k_x + ik_y) k_z$
$P_{22} = 0$	$Q_{22} = (15/32\pi)^{1/2} (k_x + ik_y)^2$
$P_{30} = (7/4\pi)^{1/2} k_z$	$Q_{30} = -(7/4\pi)^{1/2} [\kappa^2 + (5/2)(k_x^2 + k_y^2)] k_z$
$P_{31} = -(21/4\pi)^{1/2} (k_x + ik_y)$	$Q_{31} = (21/4\pi)^{1/2} (k_x + ik_y) [\kappa^2 + (5/4)(k_x^2 + k_y^2)]$
$P_{32} = 0$	$Q_{32} = (105/32\pi)^{1/2} (k_x + ik_y)^2 k_z$
$P_{33} = 0$	$Q_{33} = -(35/64\pi)^{1/2} (k_x + ik_y)^3$
$P_{40} = (9/4\pi)^{1/2} [k_z^2 - \kappa^2 - 4(k_x^2 + k_y^2)]$	$Q_{40} = (9/4\pi)^{1/2} [\kappa^4 + 5\kappa^2(k_x^2 + k_y^2) + (35/8)(k_x^2 + k_y^2)^2]$
$P_{41} = -(45/4\pi)^{1/2} (k_x + ik_y) k_z$	$Q_{41} = -(45/4\pi)^{1/2} (k_x + ik_y) [\kappa^2 + (7/4)(k_x^2 + k_y^2)] k_z$
$P_{42} = (5/4\pi)^{1/2} (9/4)(k_x + ik_y)^2$	$Q_{42} = -(5/4\pi)^{1/2} (9/4)(k_x + ik_y)^2 [\kappa^2 + (7/6)(k_x^2 + k_y^2)]$
$P_{43} = 0$	$Q_{43} = -(35/4\pi)^{1/2} (3/4)(k_x + ik_y)^3 k_z$
$P_{44} = 0$	$Q_{44} = (35/2\pi)^{1/2} (3/16)(k_x + ik_y)^4$

Since $H_{\ell m}$ is of degree $\ell - |m|$ in k_z , $P_{\ell m}$ will be of degree $\ell - |m| - 2$ and $\partial P_{\ell m} / \partial k_z$ will be of degree $\ell - |m| - 3$ in the general case. Thus, with $\ell \leq 4$, the term in brackets in the integral is of degree zero or one in k_z . We can then use

$$\int_{-\infty}^{\infty} \exp(i k_z^3/3B^3) \exp[i k_z (\kappa^2 + k_x^2 + k_y^2)/B^3] dk_z = 2B \operatorname{Ai}([\kappa^2 + k_x^2 + k_y^2]/B^2)$$

$$\int_{-\infty}^{\infty} \exp(i k_z^3/3B^3) \exp[i k_z (\kappa^2 + k_x^2 + k_y^2)/B^3] k_z dk_z = -i 2\pi B^2 \operatorname{Ai}'([\kappa^2 + k_x^2 + k_y^2]/B^2).$$

Thus, the desired matrix elements can be expressed in terms of the Airy function and its derivative, the argument being $(\kappa^2 + k_x^2 + k_y^2)/B^2$ and the coefficients being functions of κ , k_x , and k_y . Furthermore, it is now evident from inspection of Q_{lm} and P_{lm} that the absolute square of the matrix element will involve k_x and k_y only in the combination $k_x^2 + k_y^2$, substantiating the observation made earlier that the integral $\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \dots dk_x dk_y$ could be reduced to $\int_0^{\infty} \dots \pi d(k_x^2 + k_y^2)$, so that the final transition probability which started out as an eleven-fold integral, can be reduced to a single integral.

By using the asymptotic formulas $\operatorname{Ai}(z) \approx (4\pi)^{-1/2} z^{-1/4} \exp(-2z^{3/2}/3)$, $\operatorname{Ai}'(z) \approx -(4\pi)^{-1/2} z^{1/4} \exp(-2z^{3/2}/3)$ we can evaluate even these final expressions for w_{lm} . The results are tedious, but fortunately there are simple expressions for the two most important ones,

$$w_{l0} = (2l+1)(F/4\pi\kappa)(f_l/[N_l(\kappa r_0)]^2) \exp[-4\kappa^3/3B^3]$$

$$w_{l1} = l(l+1)(B^3/8\kappa^3)w_{l0}.$$

In most practical cases the exponent will be 20 or so; accordingly, w_{l1} will be only a few percent of w_{l0} . This is in accord with simple qualitative arguments that a state with $m = 0$ extends farther in the field direction than a state with $m = \pm 1$ and so would be expected to have a higher transition probability to the continuum.

Finally, we shall express the above final formulas in terms of the atomic units introduced in the first footnote. We shall indicate such units by a tilde ($\sim$) over the corresponding variable, as $\tilde{w}_{l0} = w_{l0} \div [(e^2/2a_H)/\kappa] \approx w_{l0} \div (2 \times 10^{16} \text{ sec}^{-1})$. The result, using $\tilde{\kappa} = \kappa a_H = (\tilde{E}A)^{1/2}$ in place of $\tilde{\kappa}$, is

$$\tilde{w}_{l0} = [(2l+1)/2][\tilde{F}/(\tilde{E}A)^{1/2}] \left\{ f_l/[N_l(\tilde{E}A^{1/2}\tilde{r}_0)]^2 \right\} \exp(-2\tilde{E}A^{3/2}/3\tilde{F}) \quad (1)$$

$$\tilde{w}_{l1} = [l(l+1)/4][\tilde{F}/\tilde{E}A^{3/2}] \tilde{w}_{l0}.$$

DISCUSSION

Probability per Second for Electric-Field Induced Detachment

The preceding calculation led to simple and rather convenient expressions for the probability per second, w_{lm} , for electric-field induced detachment from atomic and

molecular anions in which the electron occupies states with $\ell = 0, 1, 2, 3$ or 4. These probabilities are seen to be explicit functions of EA, the electric field strength F and the "size" of the anion (as represented by the effective range r_0 of the interaction potential). They show that the principal part of the variation in $w_{\ell m}$ arises from an exponential term [see Eq. (1)].

We used Eq. (1) for $\ell = 0$ and $m = 0$ (i.e., for s-state anions) and determined w_{00} as a function of F , EA and r_0/a_H . Figure 1 shows w_{00} as a function of F for different values of EA for $r_0/a_H = 2$ and $f = 0.01$. Similarly, Fig. 2 shows w_{00} as a function of EA for various values of F . Since f in Eq. (1) is simply a multiplicative factor, the values of w_{00} in Figs. 1 and 2 will have to be multiplied by a factor of $y/0.01$ for values y of f . A value of f between 0.1 and 0.01 is considered reasonable. The effect of r_0 on w_{00} can be seen from the data in Tables 3 and 4 for $r_0/a_H = 2$ (Table 3) and $r_0/a_H = 5$ (Table 4). The former (Table 3) values may be considered typical of atomic anions and the latter (Table 4) typical

Fig. 1. w_{00} (s⁻¹) vs F (10^6 V cm⁻¹) for various values of EA (eV); $r_0/a_H = 2$, $f = 0.01$, $\ell = 0$.

Fig. 2. w_{00} (s⁻¹) vs EA (eV) for various values of F (10^6 V cm⁻¹); $r_0/a_H = 2$, $f = 0.01$, $\ell = 0$.

TABLE 3 Values of $w_{\ell 0}$ for $\ell = 0$ and Various Combinations of EA and F;

$$r_0/a_H = 2 \text{ and } f = 0.01$$

EA (eV)	$w_{00} (s^{-1})$				
	F (10^6 V cm^{-1})				
	0.1	1	5	20	50
0.01	8.46×10^{10}	1.54×10^{12}	8.11×10^{12}	3.28×10^{13}	8.21×10^{13}
0.03	3.25×10^9	7.28×10^{11}	4.8×10^{12}	2.02×10^{13}	5.1×10^{13}
0.05	4.98×10^7	4.00×10^{11}	3.62×10^{12}	1.62×10^{13}	4.14×10^{13}
0.1	4.9×10^1	8.04×10^{10}	2.16×10^{12}	1.18×10^{13}	3.15×10^{13}
0.3	1.82×10^{-37}	8.82×10^6	2.75×10^{11}	5.65×10^{12}	1.96×10^{13}
0.5		2.80×10^1	2.04×10^{10}	2.77×10^{12}	1.40×10^{13}
1.0		5.97×10^{-18}	3.68×10^6	3.15×10^{11}	5.78×10^{12}
2.0			1.14×10^{-4}	8.01×10^8	5.63×10^{11}
3.0			2.81×10^{-18}	3.53×10^5	2.79×10^{10}

TABLE 4 Values of $w_{\ell 0}$ for $\ell = 0$ and Various Combinations of EA and F;

$$r_0/a_H = 5 \text{ and } f = 0.01$$

EA (eV)	$w_{00} (s^{-1})$				
	F (10^6 V cm^{-1})				
	0.1	1	5	20	50
0.01	9.95×10^{10}	1.81×10^{12}	9.54×10^{12}	3.86×10^{13}	9.66×10^{13}
0.03	4.31×10^9	9.64×10^{11}	6.36×10^{12}	2.68×10^{13}	6.76×10^{13}
0.05	7.17×10^7	5.75×10^{11}	5.21×10^{12}	2.33×10^{13}	5.96×10^{13}
0.1	8.2×10^1	1.34×10^{11}	3.61×10^{12}	1.98×10^{13}	5.27×10^{13}
0.3	4.44×10^{-37}	2.15×10^7	6.69×10^{11}	1.38×10^{13}	4.78×10^{13}
0.5		8.85×10^1	6.46×10^{10}	8.77×10^{12}	4.44×10^{13}
1.0		3.04×10^{-17}	1.87×10^7	1.60×10^{12}	2.94×10^{13}
2.0			1.13×10^{-3}	7.99×10^9	5.62×10^{12}
3.0			4.71×10^{-17}	5.92×10^6	4.67×10^{11}

of molecular anions. Values of $w_{\ell 0}$ for $\ell = 1, 2, 3$ and 4 have also been calculated. These calculations show that as ℓ increases, the value of $w_{\ell 0}$ decreases for a fixed EA and F. In Table 5 values of w_{10} ($\ell = 1$; p-state anions) are given for various combinations of EA and F.

TABLE 5 Values of $w_{\ell 0}$ for $\ell = 1$ and Various Combinations of EA and F;
 $r_0/a_H = 2$ and $f = 0.01$

EA (eV)	$w_{10} \text{ (s}^{-1}\text{)}$				
	F (10^6 V cm^{-1})				
	0.1	1	5	20	50
0.01	6.6×10^9	1.22×10^{11}	6.45×10^{11}	2.61×10^{12}	6.53×10^{12}
0.03	3.99×10^8	9.74×10^{10}	6.47×10^{11}	2.73×10^{12}	6.9×10^{12}
0.05	6.99×10^6	6.75×10^{10}	6.21×10^{11}	2.79×10^{12}	7.13×10^{12}
0.1	6.51	1.8×10^{10}	5.08×10^{11}	2.81×10^{12}	7.49×10^{12}
0.3	3.42×10^{-39}	2.54×10^6	1.00×10^{11}	2.17×10^{12}	7.60×10^{12}
0.5		7.08	8.7×10^9	1.30×10^{12}	6.72×10^{12}
1.0		6.06×10^{-19}	1.64×10^6	1.84×10^{11}	3.58×10^{12}
2.0			3.34×10^{-5}	5.15×10^8	4.24×10^{11}
3.0			3.98×10^{-19}	2.11×10^5	2.22×10^{10}

The present calculations show that electric-field induced detachment from mono-negative anions is negligibly small for EA $\gtrsim 1$ eV and F $\lesssim 5 \times 10^6 \text{ V cm}^{-1}$ (see Figs. 1 and 2).

Relevance to Gaseous Dielectrics

To assess the role of field-induced electron detachment in gaseous dielectrics under electrical stress, let us consider the reaction

where AX^{*-} is a transient (metastable) negative ion which dissociates (channel 2a), is stabilized (usually by collision; channel 2b) or is destroyed by autodetachment [$AX^{*-} \rightarrow AX^{(*)} + e^{(*)}$]. For pressures normally employed in practice (say, $\sim 0.5 \text{ MPa}$) the collision time, τ_{coll} , between AX^{*-} and AX (or a buffer gas molecule, Y) is of the order of 10^{-11} to 10^{-12} s, depending on AX^{*-} and Y. If AX^{*-} is stabilized with an efficiency f' at each collision with AX or Y, then the time, τ_{st} , for collisional

stabilization of AX^{-*} is

$$\tau_{st} = \tau_{coll}/f' . \quad (3)$$

If AX and Y are large molecular systems, values of f' between 0.5 and 1 are not unreasonable (see Ref. 12). Then, taking $f' = 1$, a time of $\leq 10^{-11}$ s is roughly needed for AX^{-*} to be stabilized and yield a stable AX^- in which the attached electron is bound by an energy equal to the electron affinity $EA(AX)$ of the molecule AX . If, on the other hand, dissociative attachment (channel 2a) takes place, the fragment X^- usually is stable by $EA(X)$, the electron affinity of X , if X is an atom; ~~if X is a molecular fragment, it may still require further stabilization collisionally, and the time required for this stabilization may again be taken to be $\leq 10^{-11}$ s.~~ Thus the final, stable, products AX^- and X^- of electron attachment are formed, as a rule, within 10^{-11} to 10^{-12} s of the initial electron capture event. These stabilized ions, AX^- and X^- , will drift under the influence of the electric field to the walls of the gas container and be destroyed there. The time, τ_{wall} , required for this drift to the walls is determined by the respective ionic mobilities, the distance of the ions from the walls, and the effective value of E/P . We may take as a typical average value of $\tau_{wall} \sim 10^{-5}$ s.

Hence, the probability, p' , that the electron will be detached by the electric field from the stable AX^- and X^- ions before they reach the wall is†

$$p' \approx p \tau_{wall} . \quad (4)$$

From the data in Figs. 1 and 2 and Tables 3 to 5, it is seen that for fields normally expected in practice ($\lesssim 1 \times 10^6$ V cm⁻¹) $p' \ll 1$, if $EA(AX)$ or $EA(X)$ is $\gtrsim 0.5$ eV. Thus, unless the EA of AX and X is small ($\lesssim 0.3$ eV), the process of field-induced electron detachment must be considered unimportant.

Now, it can be seen from Eq. (2) (and from many earlier discussions; see, for example, Ref. 2) that the production of the final stable ions AX^- and X^- proceeds via the intermediate state AX^{-*} . In this intermediate state the electron is bound to the molecule instantaneously very weakly and with a spectrum of binding energies. The ionization energy, $I(AX^{-*})$, of AX^{-*} varies from $-3/2$ kT to $+EA(AX)$, the value of $I(AX^{-*})$ depending on the various phases of the vibrational cycle of AX^{-*} and being closer to $-3/2$ kT than to $+EA(AX)$. It is seen from Figs. 1 and 2 and Tables 3 to 5 that w_{lo} can be very large when EA is very small. Hence, although the intermediate AX^{-*} may have a lifetime, τ_a , of $< 10^{-12}$ s, the product

$$p' = p \tau_a \quad (5)$$

†This is of course for a uniform electric field. For nonuniform electric fields both p and τ_{wall} will vary considerably depending on the field region in which the ions are formed.

can be large. In practical situations, therefore, it is most likely that it is the effect of the electric field on AX^{*-} rather than on the stable AX^- or X^- which determines the probability of field-induced detachment (i.e., the detachment of the loosely bound electron from the high-lying levels of AX^{*-} that are very sensitive to electric fields).

Finally, we note that the present calculations show that the reported rises in current at high values of E/P in many gas discharge experiments (e.g., in SF_6 at $E/P \gtrsim 100 \text{ V cm}^{-1} \text{ torr}^{-1}$) cannot be attributed to electric field-induced detachment since the electric field strengths in these studies were too low for any significant electric field-induced detachment. The reported increases in electron current in these studies, therefore, should be due to other detachment processes (electron impact-induced detachment, photodetachment, associative and nonassociative collisional detachment, detachment in anion-excited molecule collision) and possibly due to new processes which set in at high E/P values and produce fragile (attached electrons weakly bound) primary or secondary new anions. Of these, collisional detachment processes seem to be the most dominant.

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