Recombination and Escape of Ions in High-Energy Charged Particle Tracks: Computer Simulation Compared with the Analytical Model of Jaffé

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Computer simulations have been carried out of the movement due to diffusion and drift in each other's field of ions in cylindrical tracks, representative for tracks of protons in the megaelectronvolt region in nonpolar molecular liquids. The recombination and the escape of the ions from the track, in the absence and presence of external electric fields, has been calculated. The decay in time of the number of ions due to recombination in the tracks is remarkably well described by the analytical treatment of Jaffé in 1913, when the Debye−Smoluchowski rate coefficient is used. It is concluded that the Debye−Smoluchowski expression, derived for dilute solutions (single pair interactions), is also valid for large concentrations. For low and moderate fields the ion escape yields as obtained by the Jaffé treatment are unsatisfactory. In this case the field effect is observed to resemble the behavior as given by the expression of Onsager for single pairs, in agreement with earlier theoretical predictions. For very large fields the ion escape yields obtained with the Jaffé treatment are in fair agreement with those of the simulations.

I. Introduction

High-energy charged particle particles, when passing through a medium, give rise to the formation of tracks of ionizations and electronic excitations. The escape from recombination of the ions in the track, with and without an external field, has been the subject of numerous theoretical and experimental studies ever since the beginning of the century.[1−14] On one hand, the aim has been to learn about the spatial distribution of the ions in the track and therefore about the nature of the interactions of the high-energy charged particles with the medium. On the other hand, the problem is of considerable practical importance for the interpretation of the experimental data from radiation detectors based on the principle of the ionization chamber. It is only recently that computer techniques have been developed to such an extent that the dynamics of the ions in high-energy charged particle tracks can be treated by simulation of the motion of a sufficiently large number of ions.

Several approximate analytical treatments of the escape of ions from high-energy charged particle tracks have been presented through the years. In 1913 Jaffé published the first theoretical treatment on the recombination of (oppositely charged) ions in the tracks of high-energy charged particles in the absence and presence of an external field.[15] In this paper Jaffé wrote that he was inspired by the first cloud chamber pictures, published by Wilson in 1912.[16] The pictures for the α-particles showed straight, densely ionized tracks, and it is for these tracks that Jaffé developed his theory of "ionization in columns". It is the purpose of this work to study the reliability of the analytical model of Jaffé by comparison of his results with those from computer simulations.

Jaffé assumed the ions to be formed in a cylindrical geometry with a distribution of the density of the ions around the axis of the cylinder, $n(r,t=0)$, initially the same for both positive and negative ions. For the case of absence of an external field ($E = 0$), he assumed the diffusion and neutralization of the ions to be described by

$$\frac{\partial n}{\partial t} = D\left[\frac{\partial^2 n}{\partial r^2} + \frac{1}{r}\frac{\partial n}{\partial r}\right] - kn^2 \qquad (1)$$

where D is the sum of the diffusion coefficients of both ions. We see that drift of the ions due to Coulomb forces is not considered explicitly. The disappearance of ions due to neutralization is accounted for in the term $-kn^2$. Using the so-called prescribed diffusion approximation, an analytical solution could be found for the development of the density in space and time.

With an external field present the distributions of positive and negative ions move with respect to each other due to the drift in the external field, and now the recombination is calculated in the regions of space where the columns overlap, using the term kn_+n_- for the local rate of disappearance of ions. In this way Jaffé's treatment gives (a) the time depencence of the fraction of the ions surviving recombination and (b) the dependence on the external field of the fraction of ions escaping from recombination in the track, in relation to the initial spatial distribution of the ions.

The various assumptions in the Jaffé treatment are very drastic. For the cases considered, i.e., tracks in nonpolar liquids, the Coulomb interactions are very strong. Kramers, in 1952, pointed out that the drift in the mutual Coulomb fields could not be neglected, and he gave a modified treatment, where initially the diffusion was neglected altogether.[17] Mozumder, in 1971, has taken the Coulomb interaction into account by introducing a screened potential and assuming the positive ions to be on the axis of the cylinder.[18] There is, however, little hope for an exact analytical solution, because we are dealing with a large number of ions within each other's Coulomb field. Only for the problem of one pair of oppositely charged ions has an exact solution been given. In 1932 Onsager calculated the escape from recombination of a single ion pair, with and without an external field present.[19] For zero field (and infinitely fast recombination on encounter of the oppositely charged ions) he found the well-known expression for the escape of $W_{esc} = \exp(-r_c/r)$, with $r_c = e^2/4\pi\epsilon_0\epsilon_r k_B T$, often called the Onsager radius, and where e is the electronic charge, ϵ_0 the permittivity of vacuum, ϵ_r the relative permittivity of the liquid, k_B

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Boltzmann's constant, and T the temperature. For the case of an external field an exact solution is found in the form of a series. Much later, in 1978, the exact solution for the time dependence of the problem for one pair in zero field has been given by Hong and Noolandi.[20]

In the meantime also various approximate analytical treatments had been presented for spherical distributions of ions, either based on the Jaffé treatment or as an extension of the Onsager expression in order to describe the groups of ions as they occur in tracks of high-energy electrons.[18,21,22]

It is only rather recently that computer techniques have been developed to such a stage that multi-ion pair problems, as we are dealing with here, may be treated by means of simulation of the movement of the ions due to diffusion and drift in the Coulomb and external fields.[5−13] In some earlier papers we have presented results on various aspects of the recombination and escape of oppositely charged ions in the absence and presence of an electric field, in high-energy electron tracks in nonpolar liquids.[11−13] While the spatial distribution of the ions in electron tracks is rather complex, with large changes in the direction of the tracks due to large energy losses, and comparison with the analytical models did not seem very fruitful, we thought it interesting to compare simulation results with the analytical results for cylindrical distributions representative for ion tracks. We were rather surprised to see that the time dependence of the recombination in the tracks is described very well by the Jaffé treatment for a large fraction of the recombination, when the Debye−Smoluchowski rate coefficient for the reaction of oppositely charged ions is used for the recombination in the track. This indicates that the Debye−Smoluchowski rate coefficient, which is derived for dilute solutions (single pair interactions),[3−23] is also valid at high concentrations. It was also found that while the escape probability at zero field is not predicted well by the Jaffé treatment, the escape at large fields is not very much in error.

In the examples presented below we will consider ion densities that are representative for tracks of protons in the megaelectronvolt region in molecular liquids (e.g., *n*-hexane).

Application of the simulation technique, employed in this work, is limited to charge carriers that carry out a diffusive motion with a small mean free path, i.e., smaller than typically 1 nm.[11−13] For excess electrons with a large mean free path (and a large mobility), the "ballistic" movement of the electrons in the fields has to be taken into account. Effects of a large mean free path have been considered;[24−27] however, simulation calculations for large numbers of charge pairs, including the large mean free path effects, have not been carried out yet. The results presented in this work therefore apply to (nonpolar) liquids with electrons with low mobilities, such as *n*-hexane.

II. Method of Simulations

The random diffusive motion and the drift of the ions in each other's Coulomb field is calculated by the method described in refs 11−13.

III. Results and Discussion

A. External Field Zero: Kinetics. Equation 1 describes the change in time of the ion density due to diffusion and recombination in the cylinder. If we integrate over the radius, we find

$$\mathrm{d}N/\mathrm{d}t = -\int k n^2 \, \mathrm{d}r \tag{2}$$

where N is the number of ions (of one sign) per unit length of the cylinder. Using now the so-called prescribed diffusion approximation, introduced by Jaffé, which means that the distribution of the ions is Gaussian initially and remains Gaussian, we find for the decay of the number of ions, according to the Jaffé model

$$\frac{\mathrm{d}N}{\mathrm{d}t} = -\frac{kN^2}{2\pi(b^2 + 4Dt)} \tag{3}$$

where b is the initial width of the Gaussian and $D = D_+ = D_-$. (We restrict ourselves to the case of equal widths for positive and negative ions, as given originally by Jaffé. Munoz has extended the treatment to the case of different widths for the ions of different sign.[4]) We see from eq 3 that the decay can be considered as a second-order recombination with a time-dependent specific rate of reaction. Equation 3 gives on integration

$$\frac{N(t)}{N_0} = \left[1 + \frac{kN_0}{8\pi D} \ln\left\{\frac{b^2 + 4Dt}{b^2}\right\}\right]^{-1} \tag{4}$$

If we take for the specific rate of recombination k the value for homogeneous recombination in dilute solution, a remarkable agreement is found between the results obtained from the analytical solution of the Jaffé model and the simulation for a wide range of track parameters. The specific rate for this case is given by by $k = e(\mu_+ + \mu_-)/\epsilon_0\epsilon_\mathrm{r}$, where μ_+ and μ_- represent the mobilities of the ions; k can also be written as $k = 4\pi r_\mathrm{c}(D_+ + D_-)$, since $\mu_{+,-}/D_{+,-} = k_\mathrm{B}T/e$.

In Figure 1 we show the fraction of ions surviving recombination at a time t in a cylindrical track of 20 and 104 ions of each sign, for the case of an average separation between the ions in the direction of the track of $R_{++} = 3$ and 0.86 nm, respectively, and with $b = 6$ nm, with external field zero. We see that the decay of the first half of the ions is rather well predicted; however, the tails are different. In the Jaffé model the probability of escape at infinite time is always zero. For larger values of the average separation along the track the agreement is very similar. Calculations have been carried out for average separations varying from 0.5 to 9 nm.

To investigate the relative effect of diffusion and mutual fields, we have carried out simulations where the random displacements due to diffusion were taken equal to zero. In Figure 1 we see the surprising result that switching off of the diffusive displacements has hardly any effect on the kinetics. Recombination is now entirely governed by the mutual fields of the ions. Diffusion apparently does not play a role of any importance. It may be realized that with this geometry on average the Coulomb interactions are large. The root-mean-square displacement due to diffusion in 10^{-10} s for $D_+ = D_- = 1.26 \times 10^{-9}$ m^2/s is equal to $(6Dt)^{1/2} = 1$ nm, while the drift due to the Coulomb field between two ions initially at 3 nm during the same time leads to a separation of 3.3 nm. We find at this time an increase in the value of the term in the curly brackets in eq 2, and therefore of the effective specific rate of recombination, of only about 1%. We have found that for higher temperatures, where diffusion is favored with respect to drift in the field, the agreement becomes less satisfactory. It appears that the agreement is caused by the fact that the rate coefficient is independent of concentration and that the diffusion plays a negligible role.

As has been discussed in the work of ref 13, the simulated probability of ion escape from high-energy electron tracks is not significantly affected by the magnitude of D_+ and D_-, provided they are sufficiently small for the random motion of the charges to be purely diffusive. The same was found for

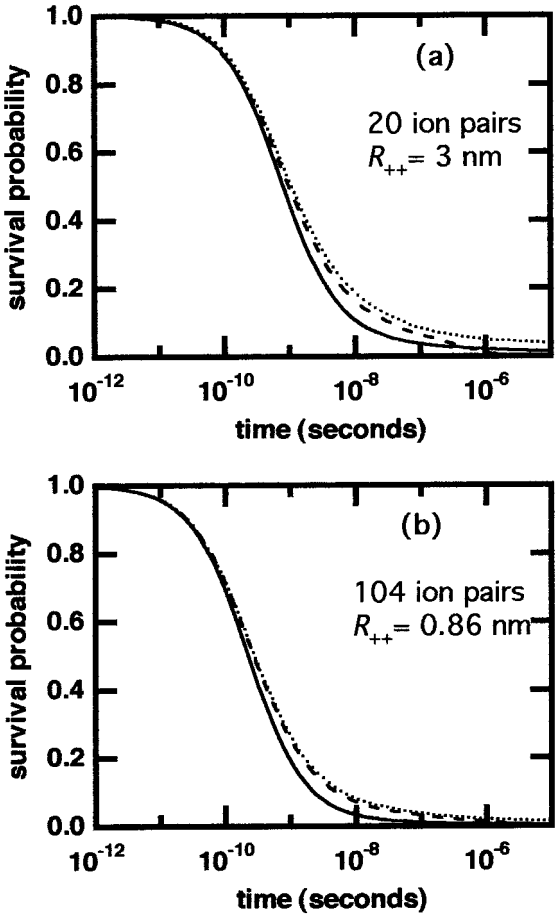

Figure 1. Probability of survival from recombination as a function of time for ion pairs in cylindrical tracks, without an external electric field present calculated (a) by the Jaffé model (drawn line), (b) by computer simulation (dotted), and (c) by computer simulation, without random displacement by diffusion (dashed) (see text). A total number of ion pairs of 20 and 104 is taken; the initial distribution of the density of the ions is taken as a cylindrical Gaussian with a width $b = 6$ nm; the average distance between the ion pairs along the track is taken as $R_{++} = 3$ and 0.86 nm, respectively. The diffusion coefficient of the ions is 1.24×10^{-9} m^2/s, the reaction radius is 0.3 nm, the temperature is 293 K, and $\epsilon_r = 2$ ($r_c = 28.5$ nm).

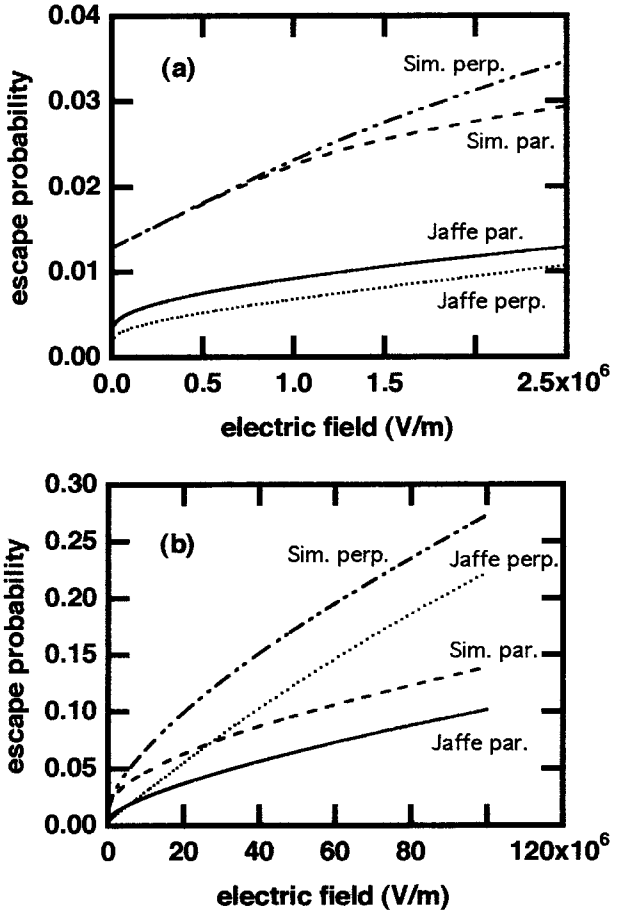

Figure 2. Probability of survival from recombination as a function of field for ion pairs in cylindrical tracks, with a moderately large external electric field present (a) and with very large fields (b), as calculated by the Jaffé model for a field parallel (drawn line) or perpendicualar (dotted line) to the track and by computer simulation for a field parallel (dashed line) or perpendicular (short and long dashes) to the direction of the track. The number of ion pairs was taken equal to 104; the initial distribution of the density of the ions was taken as a cylindrical Gaussian with a width $b = 6$ nm; the average distance between the ion pairs along the track was taken to be $R_{++} = 0.86$ nm. The diffusion coefficient of the ions was taken equal to 1.24×10^{-9} m^2/s, the reaction radius used is 0.3 nm, the temperature was taken equal to 293 K, and $\epsilon_r = 2$ ($r_c = 28.5$ nm).

tracks with a higher ion density as discussed in the present work. However, the recombination kinetics is faster as the value of $D_\pm$ increases.

The fact that the decay in the track is so well represented by the Jaffé treatment, using the Debye−Smoluchowski rate coefficient, derived for pairs of oppositely charged ions in dilute solution is intriguing, since in the track each ion undergoes strong Coulomb interactions with several other ions. Apparently, on average the recombination rate is dominated by the next-neighbor interaction, and somehow the interactions with the other ions are canceled out.

We have investigated this effect more extensively by considering the rate of reaction in homogeneous distributions of positive and negative ions (randomly distributed) as a function of the concentration of the ions. We shall show in a separate paper that also for homogeneous distributions the validity of the Debye−Smoluchowski rate coefficient is not limited to single pair interactions and may be extended to very high concentrations.

The probability of escape from recombination in zero field cannot be obtained with Jaffé's treatment as we have mentioned above, since the escape probability is always zero for the cylindrical case.

B. Escape in an External Field: Moderate Fields. In Jaffé's treatment the ions escaping recombination in the presence of a field parallel ($\Theta = 0°$) and perpendicular to the axis ($\Theta = 90°$) are considered separately. In the first case the columns of the positive and negative ions move in opposite directions along the axis; if the initial column is not infinitely long, at either end a colomn of ions of one sign will arise, which will not recombine anymore. In the overlapping part the treatment for $E = 0$ is still applicable. When the field is perpendicular to the axis, the column of the positive ions moves with respect to that of the negative ions (with axes parallel). Using the prescribed diffusion approximation, the solution of the problem is again straightforward, and the fraction of ions escaping from recombination in the track can be calculated.

In Figure 2a we show the two contributions separately for the case of 104 ion pairs initially distributed as in the Jaffé treatment, with $b = 6$ nm and with $R_{++} = 0.859$ nm. In the Jaffé treatment for $\Theta = 0°$ the escape probability decreases with increasing N_0. The upper curve for $W_{esc}(E)$ for $\Theta = 0°$ will therefore be higher for smaller N_0 and lower for larger N_0. The curve for $W_{esc}(E)$ for $\Theta = 90°$ is independent of the length of the track.

The simulation results with the same initial conditions for $\Theta = 0°$ and $\Theta = 90°$ are also given, and we see that there is no angular dependence at low fields, in contrast to Jaffé's result. This is not too surprising, considering that the ions experience very large mutual Coulomb fields. At 6 nm the Coulomb field between two ions in a dielectric liquid is 1.9×10^7 V/m. The effect of the external field on W_{esc} is mostly due to the effect on the last few ion pairs of the group, after recombination of most of the others, and the last ion pairs will have a random orientation with respect to the field. We see that at zero field the escape yield differs from zero, in contrast to Jaffé's result. The ratio of the slope to intercept of the probability of escape against field is approximately 0.8×10^{-6} m/V for fields up to about 10^6 V/m. This does not differ much from the value expected for single ion pairs, according to Onsager, which is given by $e^3/(8\pi\epsilon_0\epsilon_r k_B^2 T^2) = er_c/(2k_B T) = 0.6 \times 10^{-6}$ m/V for $r_c = 284 \times 10^{-10}$ m and $T = 300$ K. This is in agreement with the conclusion arrived at in earlier work from this laboratory[14] as well as in the work of Pimblott,[28] that, for groups of ion pairs where the probability of escape is small, for small fields the field effect is expected to be given by the Onsager expression. It must be concluded that the Jaffé treatment for moderate fields gives an escape probabilitythat is of the right order of magnitude; however, the predicted angular dependence is incorrect.

The values for the limiting value of the ratio of slope to intercept (S/I) at low fields, obtained from the calculations, may be compared with the experimental value of 0.8×10^{-6} m/V for protons in *n*-hexane with an average LET (linear energy transfer) of 11 ± 3 eV/nm.[29,30] The value of S/I found from Figure 2a is 0.8×10^{-6} m/V as mentioned above, for $R_{++} = 0.86$ nm. Using a value of 20 eV per ion pair formed initially, the LET of 11 eV/nm corresponds to $R_{++} = 1.8$ nm. Calculations have shown that the value of S/I changes negligibly over this range of values of R_{++}. We see therefore that the calculated value of S/I agrees well with the experimental result.

Other experimental results on the field dependence of the ion escape yield have been presented for ca. 5 MeV α particles in *n*-hexane,[29,30] tetramethylsilane (TMS),[4,31] and a few other saturated hydrocabon liquids[4,30] and for protons in TMS.[31] The excess electron mobility in TMS and most of the other saturated hydrocarbon liquids used is very large.[32] As we have mentioned above, for liquids with very large electron mobilities the mean free path between scatterings is very large, and the computational method used in the present work cannot be applied any more (ballistic effects need to be included).

For *n*-hexane a value for the limiting ratio S/I of $(2.1 \pm 0.4) \times 10^{-6}$ m/V for an average LET of 97 ± 20 eV/nm for 5.3 MeV α particles has been reported.[29,30] From the results for the field dependence of the ion escape yield for 5.5 MeV α particles in 2,2,4-TMP,[4] a lower limit for S/I of 1.8×10^{-6} m/V is estimated. The value of the LET for these experiments would correspond to $R_{++} = 0.2$ nm. Computer simulations of the field dependence of the ion escape for tracks consisting of 215 and 430 ion pairs with $R_{++} = 0.2$ nm gave values of S/I of 0.8×10^{-6}m/V for fields up to 10 kV/cm. The difference of more than a factor of 2 with the experimental results obtained for α particle tracks must be due to the rather simple initial track structure used in the simlations. A more detailed consideration of the initial track structure is needed to describe the ion escape from these tracks. In the case of 2,2,4-TMP the secondary electron thermalization distance is about 15 nm, which is significantly larger than in *n*-hexane. We have not carried out computer simulations for this case.

C. Escape in Large External Fields. We now turn to the escape in the presence of large external fields. In Figure 2b we show the results for the same case as considered in Figure 2a for moderate fields. We see that the Jaffé treatment results in a much larger escape for the field perpendicular than for the field parallel at large fields.

The results on the escape for the simulations for the same initial spatial distribution show a considerable difference between the field parallel and perpendicular, similar to the results of the Jaffé treatment. The absolute magnitudes of the escape probabilities are somewhat larger than those obtained with the Jaffé treatment; however, considering the simplicity of the Jaffé treatment the difference is remarkably small. In this case the diffusion is of little importance. The calculation of the recombination in the Jaffé treatment, using the Debye−Smoluchowski rate coefficient, is essentially correct. The main inaccuracies are caused by the treatment of the track ends. According to the Jaffé model, the ion escape probability decreases with the length of the track for parallel fields, which was also found to be the case for the simulations.

If the tracks have a random orientation with respect to the direction of the external field, one has to average over all orientations (Θ) with weights given by the solid angle $\sin\Theta\, d\Theta$. The averaged ion escape probability will thus lie between that for the parrallel and the perpendicular field direction, somewhat closer to that for the perpendicular field direction.

The case considered here is approximately representative for the track of a proton of around 5 MeV in a hydrocarbon liquid with a relatively small electron thermalization distance such as in *n*-hexane. The ionizations are caused by the proton and by the secondary (etc.) electrons. The vast majority of the secondaries will have an energy below a few hundred electronvolts, and therefore a large fraction of the secondary ionizations will occur within a radius of around 5−10 nm around the proton path. The proton path will be approximately straight, since large directional changes do not occur. In *n*-hexane the electron thermalization distance is about 6−8 nm. In addition to this core of dense ionization, there will be occasional side tracks due to secondary electrons with large energies. For a 5 MeV proton the maximum energy of the secondary electrons is 11 keV, with an extrapolated range on the order of 1000 nm and with an ionization density of the same order as that of the core of the track. While the results of the Jaffé treatment probably are of the right order of magnitude for such a track, for a detailed analysis of the track properties it may not be considered reliable, and simulation calculations are needed.

References and Notes

(1) *Ionization, Conductivity and Breakdown in Dielectric Liquids*; Adamczewski, I., Ed.; Taylor and Francis: London, 1969.
(2) Hummel, A. In *Advances in Radiation Chemistry*; Burton, M., Magee, J. L., Eds.; Wiley: New York, 1974; Vol. 4, Chapter 1.
(3) *Diffusion-Limited Reactions*; Rice, S. A., Ed.; Elsevier: Amsterdam, 1985.
(4) Munoz, R. C.; Cummings, B.; Holroyd, R. A. *J. Chem. Phys.* **1986**, *85*, 1104.
(5) Clifford, P.; Green, N. J. B.; Pilling, M. J. *J. Phys. Chem.* **1987**, *91*, 4417.
(6) Green, N. J. B.; Pilling, M. J.; Pimblott, S. M.; Clifford, P. *J. Phys. Chem.* **1989**, *93*, 8025.
(7) Green, N. J. B.; Pimblott, S. M. *J. Phys. Chem.* **1990**, *94*, 2922.
(8) Pimblott, S. M.; Green, N. J. B. *Radiat. Phys. Chem.* **1996**, *47*, 233.
(9) Brocklehurst, B. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 167.
(10) Brocklehurst, B. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 2823.
(11) Bartczak, W. M.; Hummel, A. *J. Chem. Phys.* **1987**, *87*, 5222.
(12) Bartczak, W. M.; Hummel, A. *J. Phys. Chem.* **1993**, *97*, 1253.
(13) Siebbeles, L. D. A.; Bartczak, W. M.; Terrisol, M.; Hummel, A. *J. Phys. Chem. A* **1997**, *101*, 1619.
(14) Tachiya, M.; Hummel, A. *Chem. Phys. Lett.* **1989**, *154*, 497.

(15) Jaffé, G. *Ann. Phys.* **1913**, *42*, 303.
(16) Wilson, C. T. R. *Proc. R. Soc. London* **1912**, *A87*, 277.
(17) Kramers, H. A. *Physica* **1952**, *18*, 665.
(18) Mozumder, A. *J. Chem. Phys.* **1971**, *55*, 3020.
(19) Onsager, L. *Phys. Rev.* **1938**, *54*, 554.
(20) Hong, K. M.; Noolandi, J. *J. Chem. Phys.* **1978**, *68*, 5163.
(21) Lea, D. E. In *Actions of Radiations in Living Cells*; Cambridge University Press: Cambridge, 1946.
(22) Dodelet, J.; Freeman, G. R. *Int. J. Radiat. Phys. Chem.* **1975**, *7*, 183.
(23) Debye, P. *Trans. Electrochem. Soc.* **1942**, *82*, 265.
(24) Tachiya, M. *J. Chem. Phys.* **1988**, *89*, 6929.
(25) Tachiya, M.; Schmidt, W. F. *J. Chem. Phys.* **1989**, *90*, 2471.
(26) Mozumder, A. *J. Chem. Phys.* **1994**, *101*, 10388.
(27) Mozumder, A. *Chem. Phys. Lett.* **1995**, *233*, 167.
(28) Pimblott, S. M. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 3533.
(29) Blanc, D.; Mathieu, J.; Vermande P.; Torres L. *Health Phys.* **1965**, *11*, 63.
(30) Mathieu J. *Etude physico-chimique de la conduction* induite par les rayonnements nucléaires dans les liquides diélectriques application a *la dosimétrie.* Thesis, Universitéde Toulouse, 1968.
(31) Ochsenbein, S.; Sass, J. In *The Liquid State and Its Electrical Properties;* NATO ASI B193; Kunhardt, E. E., Christophorou, L. G., Luessen, L. H., Eds.; Plenum Press: New York, 1988; p 554.
(32) *Handbook of Radiation Chemistry*; CRC Press: Boston, 1991.