

# Monte Carlo Simulation of Electron Thermalization Distribution in Liquid Hydrocarbons: Effects of Inverse Collisions and of an External Electric Field

Vitaly A. Rassolov\*

Department of Chemistry, Northwestern University, Evanston, Illinois 60208

A. Mozumder

Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556

Received: September 13, 2000; In Final Form: December 8, 2000

A Monte Carlo simulation has been developed for electron thermalization in a liquid hydrocarbon taking *n*-hexane as a paradigm. For the first time, both the effect of the geminate cation and that of an external electric field have been included in the predicted electron thermalization distance distribution (ETDD). Also for the first time, both energy losing (direct) and energy gaining (inverse) collisions of the epithermal electron are included in a manner that ensures the equality of their rates, averaged over the Maxwellian distribution, in the long-time limit. Parametric values have been rationalized from the experimental data. Comparison with a free-ion yield experiment in *n*-hexane at 300 K indicates that about one-third of total epithermal collisions involve the energy exchange of quanta related to intermolecular motion. These energy exchange collisions partition between energy losing to energy gaining processes approximately as 3:2 in the initial stage of thermalization. The important features of the ETDD are displacement from the origin and an exponential tail for which rationalization has been provided. Distortion of the ETDD by an external field does not affect the free-ion yield in the first order; in the second order, an effect quadratic in the field may be seen.

## I. Introduction

A key issue in radiation chemistry is a proper description of the kinetics of energy loss of electrons detached from a molecule by an ionization process. Electron thermalization is of great importance since the reactions and even the nature of thermalized versus nonthermalized electrons are usually quite different. Of the various questions related to thermalization, the most important one in the gas phase is the thermalization time, while in liquids it is the thermalization distance distribution.<sup>1–3</sup> In nonpolar liquid hydrocarbons which are otherwise insulating, ionizing radiation induces a certain conductivity attributable to the generation of liberated electrons. After thermalization, ionized electrons have a chance to escape recombination with geminate positive ions, which is predominantly determined by the initial or thermalization separation.<sup>4</sup> An understanding of the thermalization process is therefore necessary for the calculation of the electron escape probability and, hence, of the radiation induced conductivity. A closely related problem is the probability of the electron reacting with a uniformly distributed solute at a low concentration. Such scavenger reaction in a low-mobility liquid hydrocarbon is predominantly with thermalized electrons, and once again, the electron thermalization distance distribution plays an important role.<sup>5</sup>

A number of theoretical attempts to study the thermalization process have been made.<sup>6–10</sup> Some of the earlier works try to simplify the thermalization calculation and make it possible to describe the electron behavior semianalytically.<sup>6,7,10</sup> Other alternative approaches make use of Monte Carlo-type simulations for studying the shape of the electron thermalization distance

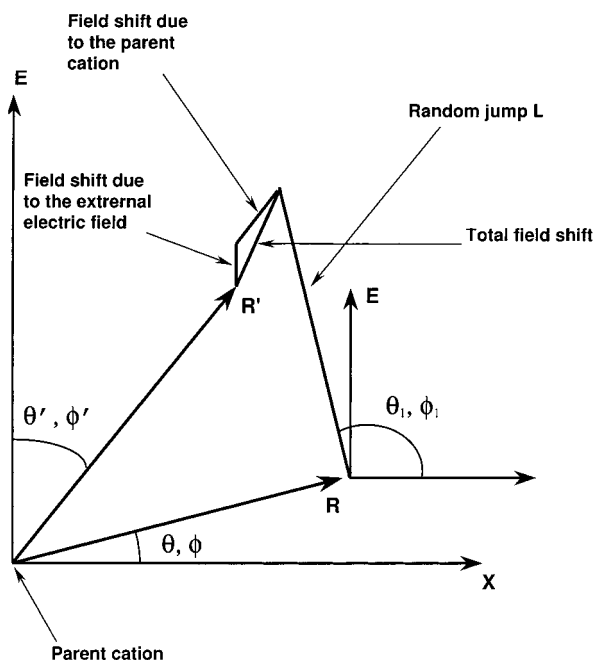
distribution (ETDD)<sup>8</sup> or the kinetics of recombination.<sup>9</sup> In these earlier calculations, only the energy loss processes of the subexcitation electrons are considered omitting the concomitant energy gain (inverse collision) processes, without which proper thermal equilibrium cannot be established. As will be shown, this latter process is important in determining the tail of the ETDD which is the dominant factor in the calculation of escape probability. In this paper we consider (1) the effect of inverse collisions during the thermalization process, (2) the calculation of the ETDD from first principles and not just the mean escape probability or fitting the ETDD to any known simple functional form,<sup>6,7</sup> and (3) the effect of an external field on the ETDD. It will be shown that the distortion of the ETDD by the external field does not affect the calculation of the Onsager escape probability in the first order (i.e., linear in the field), although a second-order effect quadratic in the field is seen.

In the following section, a description of the Monte Carlo procedure is provided, together with a discussion of the criterion used for thermalization. The next section considers the effect of an external electric field on the ETDD. This is followed by a section on results and discussion, including comparison with experiments. Finally, the conclusions are summarized.

## II. Monte Carlo Procedure: Criterion for Thermalization

Electrons become subexcitational after rapid energy loss due to ionization and excitation, when their kinetic energy falls below the first excitation potential. The energy loss rate of subexcitation electrons is greatly diminished, and it is mainly due to the excitation of intramolecular vibrations.<sup>11</sup> Mozumder and Magee<sup>6</sup> envisaged a second stage when the electron energy

\* Corresponding author. E-mail: rassolov@chem.nwu.edu.



**Figure 1.** Coordinates for Monte Carlo procedure in the field of the geminate cation and in the presence of an external electric field.

falls below a few tenths of an electron volt. For such subvibrational electrons, the mechanism of intramolecular vibration becomes very inefficient. On this stage, the electron is thermalized by the slow processes of energy exchange, the excitation of intermolecular vibrations, phonons, etc. The electron energy loss is thus subdivided into vibrational ( $E > E_v$ ) and subvibrational ( $E < E_v$ ) stages in a manner reminiscent of Platzman's<sup>11</sup> division of energy loss due to electronic excitation. The implication is that most of the thermalization range is accrued in the subvibrational stage and the ETDD would be relatively insensitive to the initial electron energy. During this last stage, the electron kinetic energy is significantly influenced by the Coulombic field of the geminate ion. Both energy loss and gain are involved in the final thermalization stage and their rates, averaged over a Maxwellian distribution, would have to be equal in the post-thermalization regime to maintain the equilibrium. While in gases both kinds of energy exchange have been considered,<sup>12–15</sup> energy gain was omitted in liquids.<sup>6–10</sup> In this paper, we consider both energy loss and gain for proper thermalization.

The procedure for Monte Carlo simulation is illustrated in Figure 1. First, the electron is placed at a predefined initial separation  $R$  from the geminate ion, making an angle  $\theta$  with respect to the external field. An initial kinetic energy  $E$  is assigned to the electron before it makes a jump. The positional shift due to a jump has two components. The random component due to kinetic motion of the electron is assumed to be isotropic, and it is simulated with a fixed jump length  $L$  and with polar and azimuthal angles  $\theta_1$  and  $\phi_1$ , found on the basis of two random numbers, as shown in Figure 1. The isotropicity of the random motion means that the electron has no memory of the direction of the previous jump and that the process is Markovian. The second component of the shift, due to the fields of the geminate ion and the external field, is computed using the thermal mobility of the electron, while the jump time is obtained from the electron kinetic energy. The total shift is the vector sum of the random and field shifts with which the new position of the electron,  $R'$  and  $\theta'$ , are calculated. Next, a random number is sampled to determine if an inelastic collision has occurred

according to a preassigned probability  $k$ . For inelastic collisions, another random number is called to determine if energy was lost or gained due to the subvibrational interaction. As explained later, the ratio of energy loss to energy gain probabilities can be found ab initio for a given value of the energy quantum; therefore, this is not an adjustable parameter. After a jump, the electron kinetic energy changes due to motion in the electrostatic fields and also due to inelastic collision if there is one. The new kinetic energy  $E'$  is thus calculated, and a criterion for thermalization, based on the Boltzmann distribution, is applied by calling yet another random number. This criterion is similar to the Metropolis method.<sup>16</sup> If thermalization is realized, the thermalization distance,  $R'$ , and  $\theta'$ , are recorded. If not, the procedure of jump and shift is continued with the new kinetic energy at the new position until thermalization has been achieved. The entire process is repeated a large number of times (typically  $10^4$ – $10^7$ ), and the statistical analysis of the results of simulation gives us the electron thermalization distance distribution (ETDD).

Electron energy at the beginning of the subvibrational stage  $E_v$  has been chosen to be 0.4 eV<sup>6</sup> which is a typical vibrational quantum of the CH bond having a frequency of about 3000  $\text{cm}^{-1}$ . The underlying assumption is that the main channel of energy absorption of subexcitation electrons in hydrocarbons is the vibration of hydrogen. In this simplified model, the intramolecular vibrations are represented by a single quantum rather than by a distribution. Later experimental work supported this approximation.<sup>10,17</sup> Thus, taking liquid *n*-hexane as a paradigm, Mozumder and Magee<sup>6</sup> computed heuristically  $R_v$ , the RMS distance between subexcitational and subvibrational energies, as 17 Å. This value is nominally identified with  $R_0$  in the present Monte Carlo procedure. However, the effect of the variation of  $R_0$  on the calculated ETDD will also be investigated. As for the quantum  $\epsilon$  of intermolecular vibrations or phonons, a value 0.01 eV was used by Mozumder and Magee,<sup>6</sup> which represented the dominant part of the Raman spectrum in liquid hydrocarbons involving small quanta, for which there is no analogue in the gas phase. The same quantum will be used in the present work. However, the ratio of the elastic to inelastic cross sections involving intermolecular vibrations will have to be different from the previous work, since we are considering both energy loss and energy gain processes. The latter is necessitated by the fact that, in the subvibrational regime, we are considering processes at near equilibrium. Therefore the total inelastic collision cross section is adjusted until the Onsager escape probability, calculated using the derived ETDD, agrees with the experimental value at a given (room) temperature, after which no more adjustment is needed.

Since the quantum  $\epsilon$  for intermolecular phonons is smaller than  $k_B T$  at room temperature, it will be necessary to take into account transitions between different levels of phonon population. According to the principle of microscopic reversibility,<sup>18</sup> the cross-sections of energy gain and loss by interaction with level  $i$  of intermolecular phonons, denoted respectively by  $\sigma_{i,g}$  and  $\sigma_{i,l}$ , are related by

$$(p^2 - 2m\epsilon)g_i\sigma_{i,g} = p^2g_{i-1}\sigma_{i-1,l} \quad (1)$$

where  $p$  is the initial electron momentum and  $g_i$  refers to the degeneracy of the  $i$ th level. The ratio of the rates of energy gaining ( $\omega_g$ ) to energy losing ( $\omega_l$ ) collisions of the electron is equal to the ratio of the products of the corresponding cross

sections and phonon state densities. Therefore

$$\frac{\omega_g}{\omega_l} = \frac{\sum_{i=1}^{\infty} \sigma_{i,g} \rho_i}{\sum_{i=0}^{\infty} \sigma_{i,l} \rho_i} \quad (2)$$

where  $\rho_i$  is the state density at level  $i$ . The numerator on the RHS of eq 2 may be expressed, in view of eq 1, as follows:

$$\sum_{i=0}^{\infty} \sigma_{i,l} \rho_{i+1} \frac{g_i}{g_{i+1}} \left( \frac{p^2}{p^2 - 2m\epsilon} \right)$$

Using the above expression, writing  $(p^2/p^2 - 2m\epsilon) = (1 - (\epsilon/E))^{-1}$ , where  $E$  is the electron kinetic energy, and recognizing that according to the Boltzmann distribution  $(\rho_{i+1}/g_{i+1}) = ((\rho_i/g_i)) \exp(-(\epsilon/k_B T))$ , one gets from eq 2

$$\frac{\omega_g}{\omega_l} = \left( 1 - \frac{\epsilon}{E} \right)^{-1} \exp\left(\frac{-\epsilon}{k_B T}\right) \quad (3)$$

It can be explicitly shown that eq 3, when used with a Maxwellian distribution of velocities, gives equality of transition rates between any two states, thus ensuring equilibrium.<sup>19</sup> Therefore, once the total inelastic collision rate is given, its partition into energy loss and gain rates is not arbitrary but is given as in eq 3.

In most earlier work on electron thermalization, the criterion used gives the final electron kinetic energy equal to or less than  $^{3/2}k_B T$ . A more proper criterion is that the electron kinetic energy would be distributed around a mean value of  $^{3/2}k_B T$  according to the Boltzmann distribution. Using this criterion, we interrogated the electron kinetic energy at the end of each jump and sampled a probability of thermalization according to the Metropolis rejection criterion,<sup>16</sup> which was originally devised for achieving Boltzmann distribution of energy in the computer simulated positions of molecules in a container.

### III. Effects of Temperature and of an External Electric Field

The free-ion yield has been measured in *n*-hexane over the temperature interval 290–350 K.<sup>20–23</sup> To compare with the measured values, our simulation of the ETDD has been carried through a similar temperature interval. The end point of simulation depends on temperature; for example, at higher temperatures, the electron does not have to lose as much energy overall, which therefore requires fewer steps. However, this effect and the dependence of the ratio of energy loss to gain rates on temperature are automatically built into the Monte Carlo routine. Other factors that change with temperature are the liquid density and the dielectric constant. Liquid *n*-hexane density at 290 K is 0.631 g cm<sup>-3</sup>, and the coefficient of linear density variation over the stated temperature interval is  $-9.77 \times 10^{-4}$  g cm<sup>-3</sup> K<sup>-1</sup>.<sup>24</sup> It is assumed that the jump length is inversely proportional to the density. The dielectric constant  $\epsilon$  is 1.89 at 290 K, with a temperature derivative of  $-0.00155$  K<sup>-1</sup>.<sup>25</sup>

The external electric field influences the ETDD in two ways. First, it imparts an additional amount of energy to the electron, which must be lost during thermalization; usually, this effect is small. Second, the drift in the electric field (see Figure 1) gives a directional bias to the ETDD, producing a distortion of the otherwise spherical distribution. To investigate this effect, we

stored each realization of thermalization on the Monte Carlo routine in an array of dimension (400,15). The first index refers to the cation-thermalized electron distance  $r$  with a resolution of 1 Å, and the second index gives the angle of the interion vector  $\theta$  with respect to the electric field with a resolution of 12°. After a sufficiently large number of realizations, the average values are given as a distribution, which may be expanded in a Legendre series as follows:

$$g(r, \theta) = \sum_n g_n(r) P_n(\cos \theta) \quad (4)$$

where  $P_n$  is the  $n$ th order Legendre function and  $g_n(r)$  are the coefficients. It is obvious that  $g_n(r) \propto E^n$ .<sup>19</sup> If the orthonormal properties of the Legendre functions are used, the coefficients are given from eq 4 as

$$g_n(r) = \frac{\int_{-1}^1 g(r, \theta) P_n(\cos \theta) d(\cos \theta)}{\int_{-1}^1 [P_n(\cos \theta)]^2 d(\cos \theta)} \quad (5a)$$

The appropriate discretization in our case may now be depicted as

$$g_n(i) = \frac{\sum_{j=1}^{15} g(i, j) P_n(\cos(12j - 6)) \sin(12j - 6)}{\sum_{j=1}^{15} [P_n(\cos(12j - 6))]^2 \sin(12j - 6)} \quad (5b)$$

subequations for each index  $i$  representing cation-thermalized electron separation, with angles measured in degrees.

One of the most important issues in radiation chemistry is the free-ion yield (100 eV–G value). If the ionization yield is known, then a probability of escaping geminate ion recombination can be calculated from the experimental free-ion yield. For an initial, i.e., thermalization, separation  $r$  of the electron from the geminate ion with the interion vector making an angle  $\theta$  with respect to the external field, this probability was given by Onsager<sup>4</sup> on the diffusion model. A form of the Onsager escape probability suitable for computer calculation, given by Mozumder,<sup>26</sup> may be expressed as

$$\Omega = 1 - e^{-\zeta(1+z)} \sum_{k=0}^{\infty} A_k(\eta) (1 + \zeta) \frac{\zeta^k}{k!} \quad (6)$$

where  $z = \cos \theta$ ,  $\zeta = (eEr/2k_B T)$ ,  $A_0(\eta) = 1 - e^{-\eta}$ , and  $A_{k+1}(\eta) = A_k(\eta) - e^{-\eta}(\eta^{k+1}/(k+1)!)$ . Here  $E$  is the external field strength,  $\eta = r_c/r$ , and  $r_c = e^2/\epsilon k_B T$  is the Onsager length. Up to the first power in the electric field, the escape probability for a given  $(r, \theta)$  is obtained from eq 6 as  $\Omega = \exp(-r_c/r)[1 + \alpha E(1 + \cos \theta)]$ , where  $\alpha = e^3/2\epsilon(k_B T)^2$ . To get the escape probability averaged over the initial distribution, we retain the ETDD in eq 4 terms up to the first power in  $E$ , i.e.,  $g(r, \theta) = g_0(r) + g_1(r) \cos \theta$ , and integrate over the polar angle. The result is

$$\frac{1}{2} \int_0^{\infty} dr e^{-r_c/r} \int_{-1}^1 d(\cos \theta) (g_0(r) + g_1(r) \cos \theta) (1 + \alpha E(1 + \cos \theta))$$

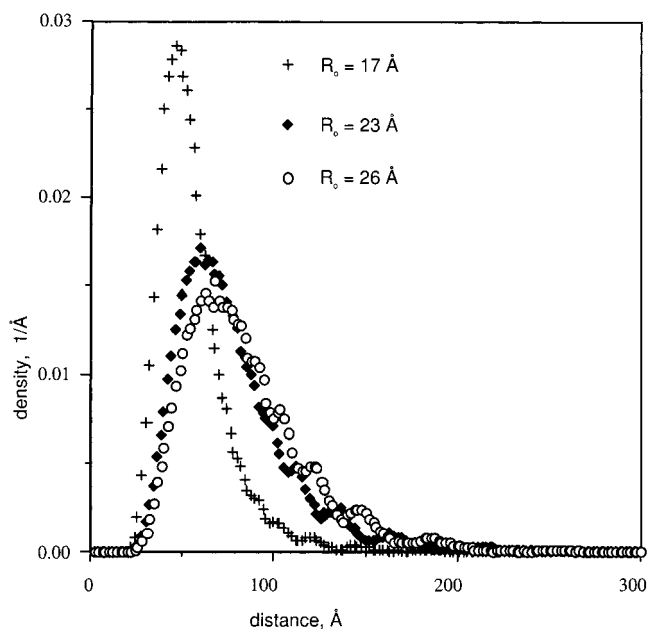
Since  $g_1 \propto E$  (see above), the integration of the above expression over  $\cos \theta$ , retaining terms up to the first power in  $E$ , gives  $g_0(r)(1 + \alpha E)$ . This means that, up to the first power in  $E$ , the distortion of the ETDD caused by the electric field

makes no contribution to the free-ion yield. Therefore, for relatively small fields, the free-ion yield should be proportional to  $E$ , and the slope-to-intercept ratio is still given by  $\alpha$  and is independent from the initial distribution, given only by the dielectric constant and the absolute temperature. This remarkable feature has been known and stressed since the early measurements of free-ion yield,<sup>27</sup> and our analysis shows that this feature remains unaltered even though the external field distorts the ETDD in the first order. Of course, the calculation of the escape probability beyond the first order in field requires the field effect on the ETDD (see the Results and Discussion section).

#### IV. Results and Discussion

This paper gives a methodology for calculating the electron thermalization distance distribution (ETDD) from first principles. For the first time, we believe, the entire ETDD is calculated and not just the probability of escaping geminate recombination (cf. ref 6). In addition, proper thermalization is achieved by taking into consideration both energy loss and energy gain for subvibrational electrons required for near-equilibrium processes. Without concomitant energy gain, the electron kinetic energy will continue to fall and will eventually go below the thermal value, unless prohibited by some artificial means. Most earlier work only considered energy loss and terminated the process when the electron kinetic energy was reduced to  $3/2 k_B T$ , or a similar amount of energy was subtracted from it right from the beginning.<sup>6–10</sup> As for the criterion of thermalization, we use a Metropolis-type method.<sup>16</sup> At the end of each jump, the electron kinetic energy  $E$  is interrogated, and a uniformly distributed random number  $R$  is called. If  $R < \exp(-E/k_B T)$ , where  $T$  is the absolute liquid temperature, the electron is considered to be thermalized, and its coordinates are stored. If not, the procedure is continued until thermalization has been achieved. For a sufficiently large number of realizations, this procedure ensures a Boltzmann distribution which could not be guaranteed in the earlier methods.

The choice of the initial values of the parameters of computation has been guided by the same considerations as in Mozumder and Magee,<sup>6</sup> except for the ratio of inelastic to elastic collision probabilities readjusted for experimental agreement<sup>20</sup> at one temperature (290 K), which is required because of the inclusion of energy-gaining collision. Notice that the further subdivision of the inelastic collisions into energy-losing and energy-gaining rates is no longer an adjustable factor but is given by eq 3. During the course of thermalization, these rates are not necessarily equal but are governed by the principle of microscopic reversibility.<sup>18</sup> At thermalization, these rates, averaged over the Maxwellian distribution, are, of course, equal.<sup>19</sup> The rationale for the initial parametric values used by Mozumder and Magee<sup>6</sup> will now be briefly recited, remembering that although the initial values are not known precisely, these cannot be changed inordinately without wholesale disagreement with the experiment. Thus the electron is considered to be subvibrational at energy  $E_0 = 0.4$  eV, the quantum of CH vibration, that being the main channel for energy exchange for the subexcitatory electron. The energy loss or quantum gain for the subvibrational electron is taken to be 0.01 eV, in accordance with the intermolecular vibration of liquid hydrocarbons as seen in the Raman spectrum. The jump length  $L$  should be comparable to the intermolecular separation and a nominal value of 5 Å is taken for  $n$ -hexane. However, our results do not show a great change for the variation of  $L$  over 4.0–6.5 Å. Extensive Monte Carlo simulations show that (1) a lower value of  $E_0$  gives a more compact ETDD without much change in the mean value



**Figure 2.** Effect of the variation of initial separation  $R_0$  on the ETDD in  $n$ -hexane. The density distribution refers to the probability of thermalization per unit spherical shell thickness. Values of other parameters are  $E_0 = 0.4$  eV,  $L = 5$  Å, and  $k = 0.325$  at  $T = 290$  K. Note that a smaller value of  $R_0$  generates a more compact distribution with a steeper peak.

and (2) a smaller value of  $k$ , the ratio of inelastic to elastic collision probabilities, results in a wider distribution.<sup>19</sup> Both effects are expected. As for the initial separation, Mozumder and Magee<sup>6</sup> argued for  $R_0 = 17$  Å on the basis of the cross sections of intramolecular vibration and the excitation of multiple quanta at each electron–molecule encounter. Since a large number of such quanta are required to bring the electron energy down from subexcitatory to subvibrational energies, it is reasonable to expect some uncertainty in the value of  $R_0$ . The result of the variation of  $R_0$  on the ETDD in liquid  $n$ -hexane is shown in Figure 2, where other parameters are fixed at their nominal values. Using our Monte Carlo simulation, we have actually obtained better agreement with experiment<sup>20,22</sup> for  $R_0 = 23$  Å, which we take as our nominal value from now on.

With parametric values as rationalized in the previous paragraph, we adjust  $k$ , the ratio of inelastic to elastic collision probabilities for subvibrational electrons in liquid  $n$ -hexane, by comparing the calculated geminate escape probability with the experiment of Schmidt and Allen<sup>20,22</sup> at 290 K in the absence of external fields. After that, no further adjustment is made. Best agreement is obtained for  $k = 0.325$ , for which the escape probability is 0.031. From eq 3, the ratio of energy loss to energy gain rates for an initial energy of 0.4 eV and  $\epsilon = 0.01$  eV is computed to be 1.429, or approximately 3:2. Therefore, the overall energy loss rate per collision is  $0.325 \times 0.01 \times (1.429 - 1.000)/(1.429 + 1.000) = 5.7 \times 10^{-4}$  eV, which compares well with the value of  $5.4 \times 10^{-4}$  eV per collision obtained by Mozumder and Magee<sup>6</sup> from comparison with a similar set of experimental data. It should be pointed out at this stage that in simulations of the kind presented here, the important factor is the product of the energy transfer quantum and the probability of overall energy loss in a collision, rather than their individual values, as was already suggested in the earlier work.<sup>6</sup>

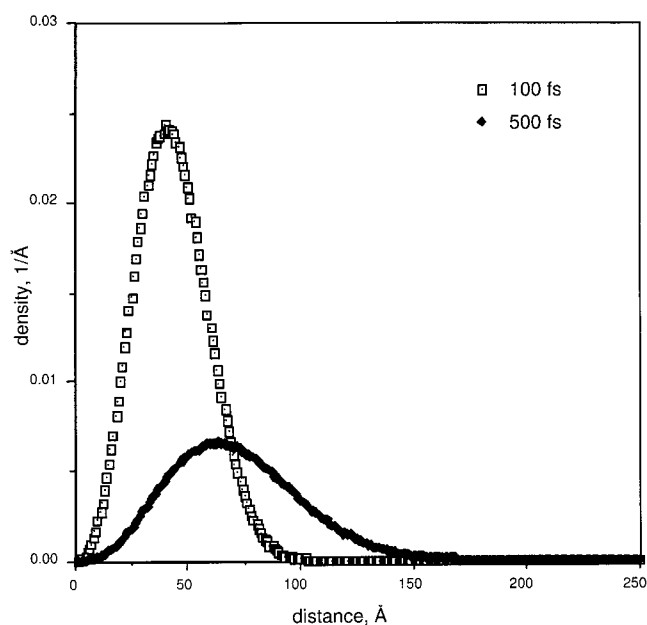
The electron thermalization distance distribution in  $n$ -hexane for a final set of parameters ( $T = 290$  K,  $k = 0.325$ ,  $L = 5$  Å,  $R_0 = 23$  Å and  $E_0 = 0.4$  eV, hereafter called the standard values of initial parameters) obtained in the present Monte Carlo



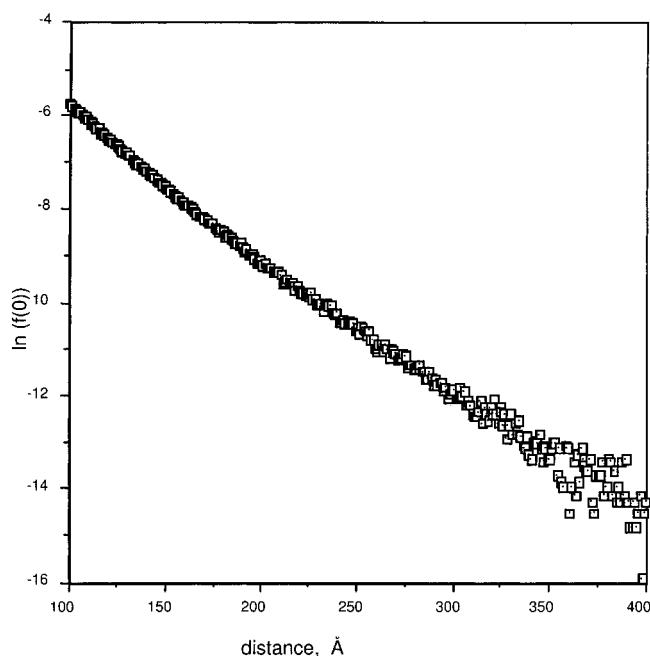
simulation method using the Metropolis criterion is shown as the middle curve in Figure 2. The density distribution refers to the probability of thermalization per unit spherical shell thickness. The minor maxima and minima at relatively large separations are probably not real but are artifacts of using a fixed quantum of energy exchange.<sup>19</sup> One of the important consequences of the results of the present work is the rationalization of certain trends in the geometrical shape of the ETDD. Several attempts have been made in the past to fit assumed empirical ETDD forms with one or two adjustable parameters to experimental results of free-ion yield and scavenging probability.<sup>28–30</sup> The forms are often different types of Gaussian, exponential, or truncated power-law functions. Relatively recent experiments of Braun et al.<sup>30</sup> suggest that the best agreement is achieved with an exponential density distribution  $\approx r^2 \exp(-\rho r)$ , which has strong support in the theory of Abell and Funabashi.<sup>28</sup> This theory treats electrons as plane waves propagating through an attenuating medium similar to the propagation of light in an opaque solution. However, the theory is somewhat inconsistent in the sense that the thermalization process is considered quantum mechanically while the post-thermal motion giving recombination or scavenging is treated classically as a diffusion process, leading to a Gaussian distribution after a large number of steps.<sup>31</sup> On the other hand, computer simulations indicate that, for relatively long times and interionic separations, the thermalization process acquires a quasistable character,<sup>19</sup> meaning that the probability of thermalization during  $t$  and  $t + dt$  in the stated limit is given to a good accuracy by  $\lambda \exp(-\lambda t) dt$ , where  $\lambda$  is a constant. The analytical shape of the ETDD in this approximation may be given by

$$g(r) = \int_{t_1}^{\infty} \exp\left(\frac{-r^2}{4Dt}\right) \frac{4\pi r^2}{(4\pi Dt)^{3/2}} \lambda \exp(-\lambda t) dt \quad (7)$$

where  $t_1$  is the time at which the electron reaches the quasistable thermalization stage. Here  $D$  is the effective diffusion coefficient given by  $L^2/6\tau$ , with  $L$  as the jump length and  $\tau$  as the jump time. To get an idea about the shape of the ETDD, we can set the lower limit of the integral in eq 7 to zero, since the integration between 0 and  $t_1$  would give a very small contribution due to the factor  $\exp(-r^2/4Dt)$  at large  $r$  in the stated limit. Equation 7 then yields  $g(r) = (\lambda r/D) \exp(-r\sqrt{\lambda/D})$  justifying the exponential character of the ETDD in the limit of long time and relatively large interionic separation. It is in this limit that theoretical calculations are best compared with experiments. Phenomena at short times or short distances are largely not detected in experiment. Note also that the nearly constant rate of thermalization cannot be obtained excluding the energy-gaining collisions in the long-time limit.<sup>19</sup> From this point of view, the spatial distribution of thermalized electrons appears as the Laplace transform of the time-dependent distribution of nonthermal electrons. Figure 3 shows the electron density as a function of electron–cation separation at 100 and 500 fs for standard values of input parameters. The distribution becomes broader at longer times with a slight shift of the peak. The outward shift of the peak is not so pronounced because of the Coulombic attraction of the cation. By about 1 to 2 ps, almost all electrons thermalize and, on the scale of Figure 3, the distribution of nonthermalized electrons become negligibly small. Figure 4 shows the logarithm of the ETDD (thermalized electrons), with standard input parameters, as a function of  $r$  for  $100 \text{ \AA} < r < 400 \text{ \AA}$ , exhibiting a nearly linear dependence. The best nonlinear least-squares fit gives a modified exponential dependence with a damping coefficient  $0.02 \text{ \AA}^{-1}$ .<sup>19</sup>



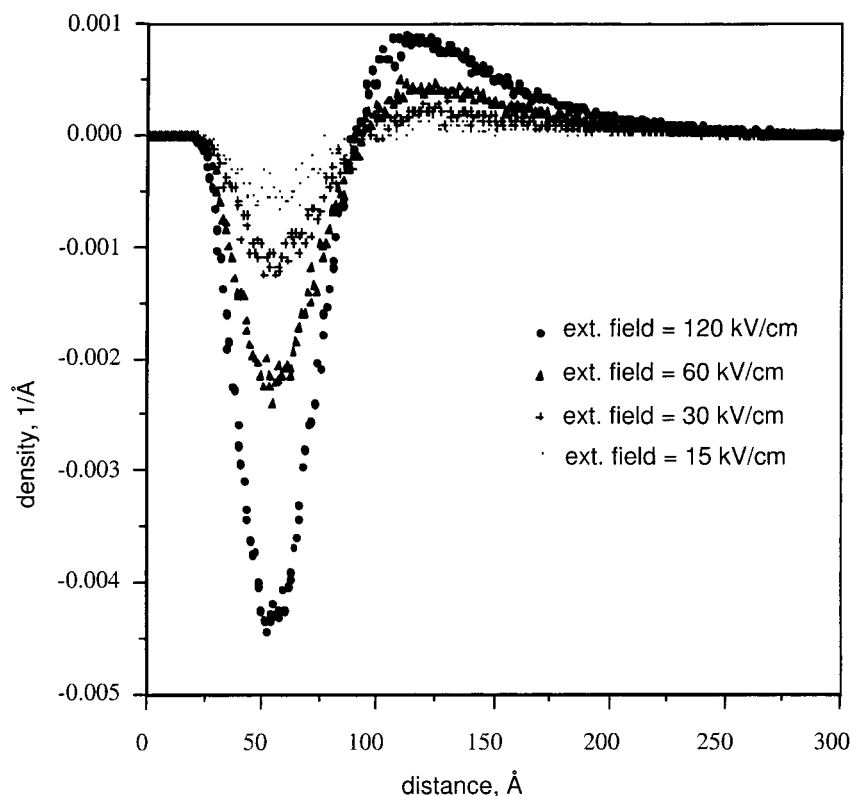
**Figure 3.** Time evolution of the radial distribution of nonthermalized electrons. See text for explanations.



**Figure 4.** Logarithm of the electron distribution thermalization distances in *n*-hexane for large electron–cation separation.

One of the common features of the ETDD is the existence of a small inner region around the cation, within which the electron cannot thermalize.<sup>21,29</sup> Originally,<sup>6</sup> it was implicitly assumed that the electron would have a small probability of thermalization within the subvibrational distance  $R_0$ . A point could be raised whether later random walk could not smooth out the hole. Our simulations, however, show that this does not happen naturally because the electron acquires too much kinetic energy in this region due to the Coulombic attraction of the cation. Consequently, there is little chance of the electron being thermalized within this inner region.

The assumptions and approximations made in this paper are quite consistent with those of earlier work in this area.<sup>6,7,9,32,33</sup> In particular, the use of thermal electron mobility during the epithermal stage, where most of the thermalization distance is accrued, deserves comment. At any time, if the electron velocity



**Figure 5.** First-order Legendre coefficient of the electron distribution thermalization distance in *n*-hexane for different external field values.  $T = 290$  K,  $k = 0.325$ ,  $L = 5$  Å, and  $E_0 = 0.4$  eV.

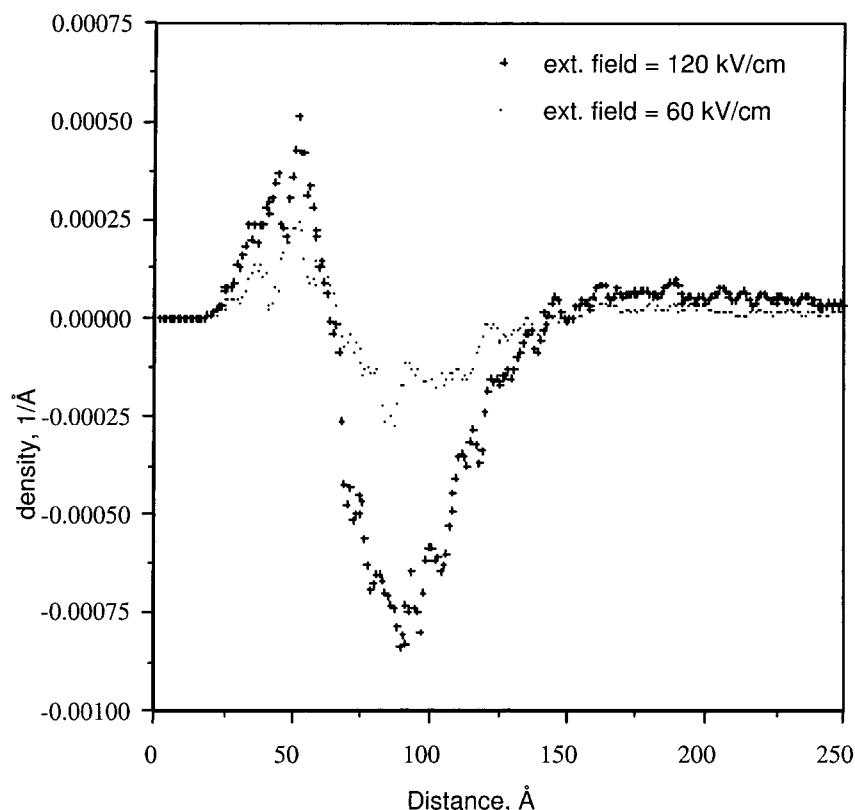
distribution and the momentum transfer cross section at a given velocity are known, then a corresponding time-dependent mobility can be evaluated.<sup>34</sup> This is quite common in thermalization work in rare gases.<sup>35,36</sup> However the relevant cross sections and distribution functions are not known for condensed molecular media, making it extremely difficult to compute the time-dependent mobility. Therefore, as is customary for thermalization in the liquid phase, we use the thermal electron mobility, and this source of error is explicitly acknowledged.

Figures 5 and 6 show respectively  $g_1(r)$  and  $g_2(r)$  the first and second-order Legendre coefficients for the effect of an external field  $E$  of different strengths on the ETDD (see eqs 4 and 5b) for standard values of initial parameters. It will be noticed that these functions, proportional respectively to  $E$  and  $E^2$  (the function  $g_0$  is the same as in Figure 2 or Figure 4), are negative in certain intervals of  $r$ . Of course, the entire distribution function  $g(r)$  always remains positive. This, however, means that the external field pulls some of the electron density at thermalization from a certain region of space and redistributes it in another place without changing the normalization. In the case of *n*-hexane, which is a low-mobility liquid, the free-ion yield is proportional to the field up to about 40 kV/cm, beyond which the dependence is sublinear.<sup>37</sup> For higher fields, the functions  $g_1(r)$  and  $g_2(r)$  would be required to compare the calculations with experiment.<sup>37</sup> Earlier calculations<sup>29,38</sup> did not consider the field effect on the ETDD and at least in one case<sup>29</sup> overestimated the escape probability at very high fields.

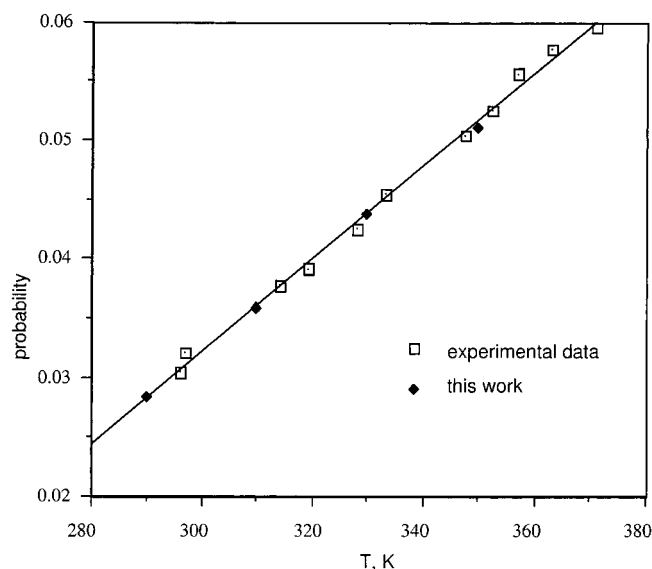
In principle, there are three kinds of experimental data that may be compared with the results on the ETDD: (1) the radiation-induced free-ion yield at low-LET (linear energy transfer) and its variation with temperature, (2) the electric field effect on the free-ion yield, and (3) the photoionization yield of a solute in liquid hydrocarbons with or without the presence of an external field. However, the consistency with experimental results itself should not be taken as a guarantee for the theoretical

procedure. For example, it has been known that an altogether unreasonable track model at low LET can give good agreement with experiment by parametric adjustment.<sup>37</sup> Therefore, our aim has been to present a theoretical model for the ETDD which captures the essential physics of the problem correctly, while paying due attention to experimental agreement. In this respect, it should be pointed out that only the parameter  $k$ , the ratio of inelastic to elastic collision probabilities, is truly adjustable. Other parameters, such as  $R_0$ ,  $E_0$ , and  $L$  can be adjusted a little, but not a great deal without wholesale disagreement with experiments.<sup>20,22,23,30,37,39</sup> This aspect has been verified by extensive Monte Carlo simulations.<sup>19</sup>

Figure 7 shows the escape probability from geminate recombination in *n*-hexane as a function of temperature over the interval 290–370 K, as obtained from the free-ion yield measurement by Schmidt and Allen using low-LET irradiation and the clearing field technique.<sup>20</sup> The result of our calculation using the Onsager escape probability at zero external field averaged over the  $R_0 = 23$  Å ETDD of Figure 2 is also shown alongside. In this calculation,  $k = 0.325$  is adjusted to give an agreement with experiment at 300 K with other values of initial parameters, as argued before and reproduced in the legend of Figure 2. (Quite similar experimental results were obtained by Schmidt and Allen<sup>22</sup> for a variety of other liquids for which similar agreement may be expected.) The temperature variation of density and the dielectric constant, as given in the first paragraph of the previous section, are built into the computation. The agreement between calculation and experimental result is well within 10–15% uncertainty of experimental determination.<sup>40</sup> Schmidt and Allen assume a Gaussian ETDD and obtain a standard deviation of 68–75 Å for  $T = 296$ –370 K by fitting into the Onsager equation. Our calculation gives an effective thermalization length 82 Å at 300 K; the difference is due to the fact that our ETDD is not assumed but calculated (see Figure 2).



**Figure 6.** Second-order Legendre coefficient of the electron distribution thermalization distance in *n*-hexane for different external field values.  $T = 290$  K,  $k = 0.325$ ,  $L = 5$  Å, and  $E_0 = 0.4$  eV.



**Figure 7.** Temperature dependence of geminate escape probability in *n*-hexane; comparison of experimental data with Monte Carlo simulation. A theoretical parameter has been adjusted only at 300 K.

In a low-mobility liquid such as *n*-hexane, the free-ion yield (or the escape probability) remains proportional to the external field with the slope-to-intercept ratio given accurately by Onsager's theory.<sup>29</sup> Beyond ca. 40 kV/cm, however, nonlinear dependence may be seen in *n*-hexane.<sup>37,41</sup> In the original work of Mathieu et al.,<sup>37</sup> Jaffe's<sup>42</sup> cylindrical track model was used for the analysis, which is not applicable to the low-LET radiation used in the experiment. As a result, too low a value (44 Å) was obtained for the effective thermalization length. In later work,<sup>41</sup> the model was corrected to Onsager's geminate recombination theory, some experimental artifact was remedied, and an

effective thermalization length 74 Å was obtained in *n*-hexane which is much closer to our calculation. According to our simulations, with the same values of initial parameters as those used for the escape probability at zero external field, a second-order dependence, viz.  $0.03 + 2.06 \times 10^{-3}E - 1.72 \times 10^{-6}E^2$ , where  $E$  is the strength of the external field in kilovolts per centimeter, gives an excellent agreement with the experimental data in *n*-hexane<sup>37,41</sup> up to the highest available field strength (160 kV/cm).

Photoionization experiments generally tend to give smaller thermalization lengths. Usually in these experiments, a solute of lower ionization potential is ionized, often in a biphotonic process, in the hydrocarbon solvent. The free-carrier yield is very low since the low probability of ionization is a contributing factor. A particularly low thermalization length of about 3 Å was obtained by Holroyd and Russel,<sup>43</sup> who use the single-photon (UV) ionization of TMPD. The thermalization length was found by using the Onsager formula without a distribution function. We are unable to rationalize such a low value but remark that it is much lower than all values found either by irradiation<sup>44</sup> or by photoionization.<sup>30,39</sup> Braun et al.<sup>30</sup> use the two-photon ionization of durene in *n*-hexane by 35 ps and 266 nm UV at 208 K. Analysis of experimental result with an exponential distribution gives a mean thermalization length 57 Å. Similar results have been obtained by Choi et al.<sup>45</sup> and by Schmidt et al.,<sup>46</sup> giving a mean thermalization length in *n*-hexane of 50–60 Å for short-wavelength excitation. Hirata and Mataga<sup>39</sup> observed the transient absorption of a solution of BDTAP in *n*-hexane at room temperature following picosecond laser pulse excitation at 280 nm and beyond. The delayed absorption is due to the cation only, and its time dependence can be attributed to the electron–cation geminate recombination process. Various forms of thermalization distribution were found acceptable by comparison with the experimental kinetics, giving

so-determined mean values. Hirata and Mataga<sup>39</sup> found that the mean thermalization length increases with photon energy. For example, the standard deviation of the Gaussian ETDD in *n*-hexane increases from 40 to 57 Å as the excess photon energy above the ionization threshold is increased from 2.0 to 3.0 eV, beyond which it stabilizes. It may be conjectured that in irradiation experiments this saturation value is being observed while the residual difference, ca. 20 Å, can be attributed to the subexcitation phase, which may be very short in photoionization experiments. The photon energy dependence of the mean thermalization length has been known for quite a long time, and a clear example has been provided by Choi et al.<sup>45</sup> Scott and Braun<sup>47</sup> observed strikingly slower recombination kinetics using the two-photon ionization of anthracene in *n*-hexane at 266 and 355 nm. Extensive results in this area were later obtained by Crowell and Bartels,<sup>48</sup> although their experiments were done in polar media. In another kind of analysis, Guelfucci et al.<sup>49</sup> use a semiempirical method for the ETDD. The method relies on fitting the experimental free-ion yield to the reciprocal of a linear function of an external field. From the fitting parameters, the moments of the ETDD with respect to the Onsager escape probability are found. The authors then conclude that a modified exponential distribution describes the UV experiments better, while for high energy irradiation, a Gaussian distribution is called for.

## V. Conclusions

1. Approximately one-third of the collisions of epithermal electrons in liquid *n*-hexane involve energy exchange of about 0.01 eV. These divide into energy-losing and energy-gaining processes roughly as 3:2.

2. The electron thermalization distance distribution has a hole around the geminate cation and a nearly exponential tail beyond ca. 100 Å.

3. The distortion of the thermalization distance distribution by an external field affects the free-ion yield in the second-order  $O(E^2)$ , which can be seen at very high fields.

**Acknowledgment.** V.A.R. acknowledges the support of U.S. Department of Energy.

## References and Notes

- (1) La Verne, J. A.; Mozumder, A. *Radiat. Phys. Chem.* **1984**, *23* (6), 637.
- (2) Hummel, A. *Advances in Radiation Chemistry*; Wiley: New York, 1974; pp 1–102.
- (3) Lukin, L. V. *Radiat. Phys. Chem.* **1992**, *40*, 565.
- (4) Onsager, L. *Phys. Rev.* **1938**, *54*, 554.
- (5) Rzad, S. J.; Infelta, P. P.; Warman, J. M.; Schuler, R. H. *J. Chem. Phys.* **1970**, *52*, 3971.
- (6) Mozumder, A.; Magee, J. L. *J. Chem. Phys.* **1967**, *47*, 939.
- (7) Sano, H.; Mozumder, A. *J. Chem. Phys.* **1977**, *66*, 689.
- (8) Goulet, T.; Patai, J.-P.; Jay-Gerin, J.-P. *J. Phys. Chem.* **1990**, *94*, 7312.
- (9) Bartczak, W. M.; deHaas, M. P.; Hummel, A. *Radiat. Phys. Chem.* **1991**, *37*, 401.
- (10) Christophorou, L. G.; Grant, K. S.; Baird, J. K. *Chem. Phys. Lett.* **1975**, *30*, 104 and references therein.
- (11) Platzman, R. L. *Radiation Res.* **1955**, *2*, 1.
- (12) Mozumder, A. *J. Chem. Phys.* **1980**, *72*, 1657.
- (13) Mozumder, A. *J. Chem. Phys.* **1982**, *76*, 3277.
- (14) Shizgal, B. *J. Chem. Phys.* **1983**, *78*, 5741.
- (15) Shimamura, I. *Phys. Rev. A* **1981**, *23*, 3350.
- (16) Metropoulos, N.; Rosenbluth, A. W.; Rosenbluth, N. M.; Teller, A. H.; Teller, E. *J. Chem. Phys.* **1953**, *21*, 1087.
- (17) Lukin, L.; Tolmachev, A.; Yakovlev, B. *High Energy Chem.* **1987**, *21*, 357.
- (18) Ross, J.; Light, J. C.; Schuler, K. In *Kinetic Processes in Gases and Plasmas*; Hochstim, A. R., Ed.; Reentry Physics Series; Academic Press: New York, 1969.
- (19) Rassolov, V. A. Master's thesis, University of Notre Dame, South Bend, IN 1991.
- (20) Schmidt, W. F.; Allen, A. O. *J. Phys. Chem.* **1968**, *72*, 3730.
- (21) Freeman, G. R. *J. Chem. Phys.* **1967**, *39*, 2822.
- (22) Schmidt, W. F.; Allen, A. O. *J. Chem. Phys.* **1970**, *52*, 2345.
- (23) Dodelet, J.-P.; Shinsaka, K.; Kortsch, U.; Freeman, G. R. *J. Chem. Phys.* **1973**, *59*, 2376.
- (24) American Petroleum Institute. *Selected Values of Properties of Hydrocarbons*; Research Project 44; Thermodynamics Research Center: College Station, TX, 1967.
- (25) Lide, D. R., ed., *CRC Handbook of Chemistry and Physics*, 78th ed.; CRC Press: Boca Raton, FL, 1997.
- (26) Mozumder, A. *J. Chem. Phys.* **1974**, *60*, 4300.
- (27) Mozumder, A. *Fundamentals of Radiation Chemistry*; Academic Press: San Diego, CA, 1999; Chapter 9.5.
- (28) Abell, G. C.; Funabashi, K. *J. Chem. Phys.* **1973**, *58*, 1079.
- (29) Mozumder, A. *J. Chem. Phys.* **1974**, *60*, 4305.
- (30) Braun, C. L.; Smirnov, S. N.; Brown, S. S.; Scott, T. W. *J. Phys. Chem.* **1991**, *95*, 5529.
- (31) Magee, J. L. *Can. J. Chem.* **1977**, *55*, 1847.
- (32) Rips, I.; Silbey, R. J. *J. Chem. Phys.* **1991**, *94*, 4495.
- (33) Yakovlev, B. S. *Radiat. Phys. Chem.* **1992**, *40*, 37.
- (34) Huxley, L. G. H.; Crompton, R. W. *The Diffusion and Drift of Electrons in Gases*; Wiley: New York, 1974.
- (35) Tembe, B. L.; Mozumder, A. *J. Chem. Phys.* **1984**, *81*, 2492.
- (36) Shizgal, B.; McMahon, D. R. A.; Viehland, L. A. *Radiat. Phys. Chem.* **1989**, *35*, 34.
- (37) Mathieu, J.; Blanc, D.; Caminade, P.; Patai, J. P. *J. Chem. Phys.* **1967**, *64*, 1679.
- (38) Terlecki, J.; Fiutak, J. *Radiat. Phys. Chem.* **1972**, *4*, 469.
- (39) Hirata, Y.; Mataga, N. *J. Phys. Chem.* **1991**, *95*, 1640.
- (40) Allen, A. O. *Yields of Free Ions Formed in Liquids by Radiation*; NSRDS-NBS 57; U. S. Department of Commerce: Washington, DC, 1976.
- (41) Cassanovas, J.; Grob, R.; Blanc, D.; Brunet, G.; Mathieu, J. *J. Chem. Phys.* **1975**, *63*, 3673.
- (42) Jaffe, G. *Ann. D. Physik* **1913**, *42*, 303.
- (43) Holroyd, R. A.; Russel, R. L. *J. Phys. Chem.* **1974**, *78*, 2128.
- (44) Gee, N.; Sennanayake, P. C.; Freeman, G. R. *J. Chem. Phys.* **1988**, *89*, 3710.
- (45) Choi, H. T.; Sethi, D. S.; Braun, C. L. *J. Chem. Phys.* **1982**, *77*, 6027.
- (46) Schmidt, K. H.; Sauer, J. M. C.; Lu, Y.; Liu, A. *J. Phys. Chem.* **1990**, *94*, 244.
- (47) Scott, T. W.; Braun, C. L. *Chem. Phys. Lett.* **1986**, *127*, 501.
- (48) Crowell, R. A.; Bartels, D. M. *J. Phys. Chem.* **1996**, *100*, 17940.
- (49) Guelfucci, J. P.; Filey-Rey, J.; Cassanovas, J.; Baird, J. K. *J. Chem. Phys.* **1997**, *106*, 9497.