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Electron thermalization distances and free-ion yields in dielectric fluids: Effect of electron scavengers

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Free-ion yields were measured in isobutane and in solutions containing sulfur hexafluoride, at densities from the liquid at 295 K to the supercritical fluid. A modified Onsager model was used to estimate the most probable thermalization distances b_{GP} (GP denotes a Gaussian power-law distribution). The density-normalized distance $b_{\mathrm{GP}}d$ in isobutane increased from 6.3×10^{-6} kg/m^2 at 295 K to a maximum of 10.5×10^{-6} kg/m^2 at 395 K, and then decreased to 5.6×10^{-6} kg/m^2 at 408 K (T_c). The maximum, which is evidence of conduction-band enhancement of b_{GP}, was suppressed in solutions containing small amounts of SF_6. The SF_6 captured the electrons while they were still at epithermal energies, and terminated their flight away from their sibling ions. The values of b_{GP} and the free-ion yields were thereby decreased.

I. INTRODUCTION

Absorption of ionizing radiation by a molecule in a dense fluid gives[1]

$$M \rightsquigarrow [M^{+}+e^{-}]\ . \tag{1}$$

The wavy arrow indicates the ionization process. The square brackets indicate that the Coulombic attraction between cation and electron is significant compared with thermal energy kT. The electron initially has excess energy. As it moves away from the cation it undergoes energy-loss interactions with the fluid molecules, and eventually becomes thermalized at a distance y from the cation. The magnitude of y and of the dielectric constant ϵ of the intervening fluid determine the probability that the thermalized electron will be drawn back to its sibling cation (geminate neutralization), or that it will escape by diffusion into the bulk medium (free-ion formation). The free ions are collectible at electrodes.

Experimentally, the thermalization distance is estimated from measured free-ion yields. The major part of y is traveled while the electron is at subvibrational excitation energies,[2,3] skittering along in the conduction band.[4–6] The thermalization distance is longer in liquids of more spherelike molecules than in liquids of more rodlike molecules,[6–8] because the energy surface of the conduction band is less undulating and scatters electrons less strongly in liquids of the former. The effect of the band is largest at a temperature near but less than T_c (subscript c denotes critical fluid).[4–6,9,10]

At 295 K addition of an electronegative solute shortens the thermalization distance.[7(b),8(b),11,12] The value of y decreases with increasing concentration of an efficient scavenger such as oxygen or sulfur hexafluoride, because the electrons can be scavenged before completion of their normal thermalization paths.[7(c),8(b),11,13]

In purified liquid isobutane, changes in the conduction band at temperatures between 295 K and $T_c=408$ K strongly affect electron transport in the fluid.[14] The present work examines the effect of an electron scavenger on thermalization distances in the liquid under these conditions.

II. EXPERIMENTAL

A. Materials

Isobutane (Phillips Research Grade, purity greater than 99.90%) was further purified in a grease-free vacuum line. The sample was passed directly from the cylinder, via a regulator and stainless steel—Kovar-glass seal, into the glass vacuum line. Following trap-to-trap distillation, where the receiver was held at 77 K and open to vacuum, the sample was held as a liquid at 293±2 K on freshly activated Davison 4A or 5A Molecular Sieves for more than 36 h. The sample was degassed again by trap-to-trap distillations, then transferred onto a sodium-potassium alloy where it was stirred for 3—4 days and kept until use.

Sulfur hexafluoride, SF_6 (Matheson Instrument Grade, 99.99% purity) was transferred at greater than atmospheric pressure through 30 cm of vacuum hose (4-mm-thick rubber) into the vacuum line. The line was flushed with SF_6. A sample was then introduced and degassed, after isolation in the vacuum line, by trap-to-trap distillations. The amount of SF_6 put into a conductance cell was measured by P and T in a 69.0-cm^3 bulb. The bulb had been previously heated to 473 K while open to vacuum. The SF_6 was condensed into the conductance cell at 77 K. An amount of isobutane was then added such that the total number density in the supercritical fluid equalled that of pure isobutane, $n_c=2.3\times10^{27}$ molecules/m^3.

B. Cells

The cells have been described.[6,9] The ~1-cm-thick glass walls can contain pressures up to ~6 MPa (~60 bars). The charge collection volume was determined from the drift distance, measured with precision calipers (Do

All, model *M*-1 minus), and the cell capacitance measured using an Electro-Scientific Industries Model 273 capacitance bridge and a General Radio Model 1422CD precision capacitor. Four different cells were used, all with collection areas of ~ 2.5 cm^2, drift lengths of ~ 0.3 cm and hence collection volumes of ~ 0.8 cm^3. The actual dimensions of the areas and distances were determined to $\sim \pm 1\%$.

C. Measurements

The measurement circuit is described in Fig. 4 of Ref. 9. The collected charge is obtained by integration of the electron and ion drift currents.

The temperature was varied using a heat gun (Master Appliances model H67518 or model AH-301) fitted to a glass tube that passed the gas through an insulating lid into the Dewar holding the conductance cell. The temperature was controlled as in Ref. 9 or by a modified Microscan 1300 (Sybron-Taylor) with a platinum-resistance sensor. The temperature was monitored near the plates and at up to three other points on the cell body using copper-Constantan thermocouples (Thermoelectric Canada Ltd., type t special) in combination with a Fluke 2100A digital thermometer. The temperature uncertainties were ± 0.5 K over the range 295—380 K, then increasing gradually to ± 0.7 K at 450 K.[15] The drift on the Fluke 2100A was ± 0.1 K for 88% of 121 calibration readings covering 73—673 K over a 1.5-year period. The maximum error was 0.3 K.

The applied voltage sources were Fluke 408B (to ± 6 kV) and Spellman DC High Voltage (for greater than ± 6 kV). The output was measured by a Fluke 8810A digital voltmeter that had a 90-day stability of $\pm 0.01\%$.

Nine sets of free-ion yields were collected using positive and negative applied voltages. The difference between the different polarity data was 1.4—5.5% with an average of 2.7%; no consistent ordering of one polarity set towards the other was observed.

D. Dosimetry

An electron beam from a 1.7-MeV Van de Graaff generator was stopped in a 3-mm-thick gold target, producing x rays that delivered $\sim 0.6 \times 10^{10}$ or 6×10^{10} eV/g to the liquid sample in 0.1 or 1.0 μs, respectively. For each pulse a dose monitor measured the charge deposited on the target by the electron beam. The monitor was calibrated each day by LiF crystals. The crystals in turn were calibrated by the Fricke dosimeter for high-density samples, and by ionization in air for low-density samples.[6] Conversion to dose absorbed in isobutane solutions at different densities was done with the aid of the Bethe equation.[16] The appropriate mean-ionization potentials were estimated[17] to be 69 eV for the Fricke solution, 52 eV for isobutane, 85 eV for air, and 137 eV for SF$_6$. The dosimetry was density dependent, probably due to wall effects, and it was interpolated linearly with electron density between the Fricke and air values.[6]

E. Physical properties

Isobutane liquid densities were obtained from Ref. 18. Dielectric constants were calculated from the Lorenz-Lorentz equation,[19] using the refractive index from Ref. 20. Sulfur hexafluoride dielectric constants were calculated from the Clausius-Mosotti equation,[21] using the low density $\epsilon - 1$ (p. 348 of Ref. 21) as a basis.

The solubility of SF$_6$ in nonpolar solvents is low, typically $\lesssim 0.1$ mol % at 295 ± 2 K, and decreases with increasing T.[22–24] In the present work, the SF$_6$ is assumed to be uniformly distributed throughout the conductance cell. Solution properties are taken as linear functions of mole fraction.

III. RESULTS

A. Electric field effect

Following generation of the electron-cation pair and thermalization of the electron [Eq. (1)], geminate neutralization

$$[M + e^-] \rightarrow M \;, \tag{2}$$

or free-ion formation

$$[M + e^-] \rightarrow M^+ + e^- \tag{3}$$

can occur. The yield of Eq. (1), G_{tot}, is the number of ion pairs initially formed per 100 eV of energy absorbed by the fluid. In the absence of an applied field the probability of free-ion (fi) formation ϕ_{fi}^0 is[25]

$$\phi_{\text{fi}}^0 = \exp(-r_c/y) \;, \tag{4}$$

where $r_c = \xi^2/4\pi\epsilon_0\epsilon kT$ is the distance (in m) at which the Coulombic attraction between the ion and electron equals the average thermal energy kT (in J), ξ is the protonic charge (in C), ϵ_0 is the permittivity of vacuum, and ϵ is the dielectric constant of the fluid between the ion and electron. The free ions diffuse independently of each other in the bulk fluid and eventually undergo homogeneous, random recombination,

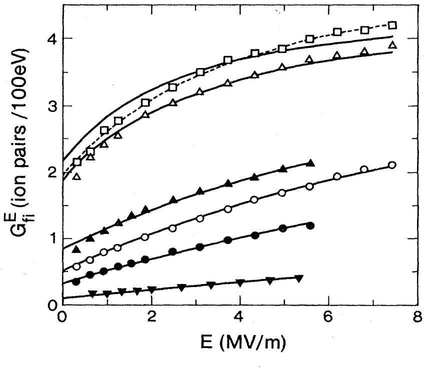

FIG. 1. Electric field dependence of free-ion yields. The following numbers represent (T, K; [SF$_6$], 10^{24} molecules/m^3): ○ (296;0), △ (399;0), □ (404;0), ● (298;3.34), ▲ (395;3.34), ▼ (298;219). The curves were calculated from Eq. (7), using parameter values from Tables I and II. The solid curves are for $G_{\text{tot}} = 4.7$, and the dashed curve is for $G_{\text{tot}} = 5.5$.

TABLE I. Parameter values for isobutane.

T (K)	d (kg/m^3)[a]	ϵ[b]	G_{fi}^0[c]	b_{GP} (nm)	$b_{\mathrm{GP}}d$ (10^{-6} kg/m^2)
295	554	1.74	0.51[d]	11.6	6.4
298	553	1.73	0.45	10.9	6.0
318	526	1.68	0.58	12.1	6.4
321	518	1.68	0.66[d]	12.9	6.7
330	510	1.66	0.66	12.7	6.5
350	478	1.62	0.94[d]	15.6	7.5
359	462	1.59	0.85	14.4	6.7
371	438	1.55	1.02	16.4	7.2
388	393	1.50	1.53[d]	23.1	9.1
393	378	1.49	1.49	22.5	10.8
399	347	1.43	1.87[d]	29.7	10.3
403	315	1.38	1.75[f]	26.3	8.3
404	309	1.38	1.95[d,f]	26.4	8.2
			(2.15)[d,g]	(36.2)[g]	(11.2)[g]
408[e]	222	1.26	1.47[d]	25.2	5.6
414[e]	222	1.26	1.59[d]	26.9	6.0
420[e]	222	1.26	1.55[d]	25.8	5.7

[a] Reference 18.

[b] Dielectric constant, see Sec. II E.

[c] $G_{\mathrm{tot}}=4.7$.

[d] Average of positive and negative applied voltage results; other data positive voltage.

[e] $T \geq T_c$.

[f] $G_{\mathrm{tot}}=5.0$ (403 K) or 5.5 (404 K).

[g] Assuming $G_{\mathrm{tot}}=4.7$, which does not fit the models at this temperature. See Fig. 1.

TABLE II. Parameter values for isobutane-SF_6 mixtures.[a]

T (K)	mol % SF_6	d (kg/m^3)[b]	ϵ[b]	G_{fi}^0[c]	b_{GP} (nm)	$b_{\mathrm{GP}}d$ (10^{-6} kg/m^2)
		$[SF_6]=3.34\times10^{24}$ molecules/m^3				
298	0.058	553	1.74	0.32	9.0	5.0
366	0.073	443	1.57	0.59	11.3	5.0
395	0.087	371	1.46	0.83	14.0	5.2
408	0.15	222	1.26	1.21	21.0	4.7
412	0.15	222	1.26	1.23	21.1	4.7
		$[SF_6]=2.74\times10^{25}$ molecules/m^3				
363	0.61	463	1.59	0.45	9.6	4.4
392	0.74	382	1.47	0.61	11.5	4.4
408	1.2	217[d]	1.26	0.99	17.9	3.9
411	1.2	217[d]	1.26	0.99	17.7	3.8
		$[SF_6]=1.13\times10^{26}$ molecules/m^3				
338	1.8	511	1.65	0.22	7.0	3.6
380	2.2	430	1.52	0.33	8.2	3.5
408	4.9	239	1.26	0.64	13.3	3.2
411	4.9	239	1.26	0.64	13.2	3.2
		$[SF_6]=2.19\times10^{26}$ molecules/m^3				
298	3.8	585	1.73	0.100	5.5	3.2
335	4.1	552	1.69	0.155	6.0	3.3
376	5.0	457	1.54	0.24	7.1	3.2
409	9.5	254	1.26	0.50	11.5	2.9
412	9.5	254	1.26	0.50	11.4	2.9

[a] Assumes SF_6 uniformly distributed in cell.

[b] Assumes linear dependence on mol %.

[c] $G_{\mathrm{tot}}=4.7$.

[d] Cell underfilled by 3%.

$$M^+ + e^- \rightarrow M \ . \tag{5}$$

Application of an electric field allows collection of the free ions at the electrodes.

$$\begin{aligned} &M^+ \rightarrow \text{cathode} \ , \\ &e^- \rightarrow \text{anode} \ . \end{aligned} \tag{6}$$

If fields of strength $E \sim 10^6$ V/m are used in liquids, the free-ion yield G_{fi}^E increases with E.[26]

At low fields homogeneous recombination [Eq. (5)] competes with ion collection. This causes the measured ion yield to approach zero as E goes to zero.[6,27]

Free-ion yields measured in liquid isobutane at three temperatures, at the equilibrium vapor pressures, are shown in Fig. 1. Similar measurements were made at other temperatures listed in Table I.

B. Scavenger effect

Addition of a small amount of SF_6 sharply decreased G_{fi}^E (Fig. 1). At 298 K values of G_{fi}^E in the solution containing 0.058 mol % SF_6 (3.34×10^{24} molecules/m^3) are half of those in purified isobutane. A further 66-fold increase in SF_6 concentration to 2.19×10^{26} molecules/m^3 only decreased G_{fi}^E a further 3-fold (Fig. 1 and Table II). Similar behavior occurs at 397 ± 2 K, which is 9 ± 2 K below the critical temperature.

IV. DISCUSSION

A. Electric field effect

In the presence of an applied field of strength E, the probability ϕ_{fi}^E that an ionization event produces free ions is[6,25]

$$\begin{aligned} \phi_{\text{fi}}^E &= G_{\text{fi}}^E / G_{\text{tot}} \\ &= \int_0^\infty F(y) \phi_{\text{fi}}^0 [1 + f(E,y,T)] dy \ , \end{aligned} \tag{7}$$

where $F(y)dy$ is the fraction of electrons that have thermalization distances between y and $y+dy$, and $f(E,y,T)$ is the fractional increase of G_{fi} caused by the field E,[6]

$$f(E,y,T) = e^{-\beta y} \sum_{n=1}^{\infty} \frac{(\beta y)^n}{(n+1)!} \sum_{j=0}^{n-1} (n-j) \frac{(r_c/y)^{j+1}}{(j+1)!} \ , \tag{8}$$

where $\beta = \xi E/kT$ and E is in V/m.

The form used for the distribution function $F(y)$ is[6,26]

$$F(y) = \begin{cases} 0.96 YG, & y < 2.4 b_{\text{GP}} \\ 0.96[YG + 0.5(b_{\text{GP}}^2/y^3)], & y > 2.4 b_{\text{GP}} \end{cases} \tag{9}$$

where 0.96 is a normalization factor, $YG = (4y^2/\pi^{1/2} b_{\text{GP}}^3) \exp(-y^2/b_{\text{GP}}^2)$, and b_{GP} is the dispersion parameter and most probable value of the thermalization distance y.

Equation (7) was fitted to the data in Fig. 1. The values of the parameters so obtained are listed in Table I, along with those from runs at other temperatures. The value $G_{\text{tot}} = 4.7$ was adequate for all data sets except those at 403 K and 404 K, where somewhat larger values were required (Fig. 1 and Table I). The true value of G_{tot} probably does not change in this narrow temperature zone; perhaps the form of the $F(y)$ distribution becomes more skewed due to changes in the scattering properties in the liquid caused by the large density fluctuations just below the critical point. Our method of analysis forced all changes to appear only in b_{GP} and G_{tot}. There are not enough data to effectively pursue a change in $F(y)$.

B. Density (temperature) effect

If the net electron-molecule interactions were independent of fluid density, the product of the thermalization distance and the density, $b_{\text{GP}} d$, would be constant.[4,8,28] However, in pure isobutane $b_{\text{GP}} d$ goes through a maximum at $T = 395$ K (Fig. 2), which corresponds to $d = 366$ kg/m^3. The density normalized mobility $n\mu$ of thermal electrons also goes through a maximum in this region, at $T = 398$ K and $d = 350$ kg/m^3 ($n = 3.6 \times 10^{27}$ molecules/m^3).[14] Both maxima are attributable to density effects that produce a scattering minimum in the conduction band. The scattering minimum is associated with a minimum in the density dependence of the conduction-band energy dV_0/dn.[29–31]

The near coincidence of the conditions for the maxima of the electron thermalization distance and the thermal electron mobility supports the suggestion that the main portion of the thermalization distance is attained while the electron is skittering along in the conductance band, at energies below a few tenths of an eV.[2,5,6,9]

The relative size of the maximum in $b_{\text{GP}} d$ in isobutane (Fig. 2) is larger than that in ethane, but smaller than that in methane.[6] It correlates with the degree of sphericity of the molecules, and therefore the relative smoothness of the conduction-band potential surface.

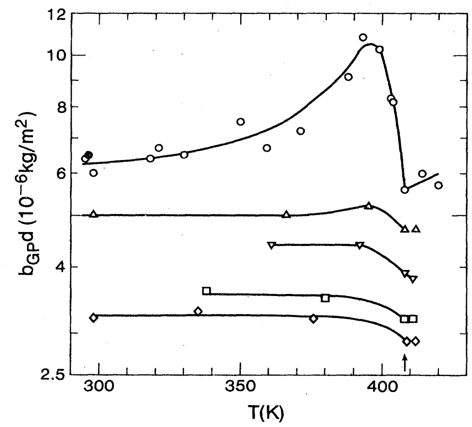

FIG. 2. Density-normalized thermalization distance $b_{\text{GP}} d$ plotted against the temperature of the liquid under its vapor pressure and of the supercritical gas at the critical density. The fluid densities are given in Tables I and II. The arrow marks T_c. The concentrations of SF_6 are (10^{24} molecules/m^3): ○, zero; ●, zero (Ref. 28); △, 3.34; ▽, 27.4; □, 113; ◇, 219.

C. Electron scavenger effect

The addition of 0.1 mol % of electron scavenger decreased $G_{\rm fi}^{E}$ (Fig. 1). Presumably $G_{\rm tot}$ was not affected. It is concluded that the electrons became attached to molecules while hot, before attaining their full thermalization distance. The value of $b_{\rm GP}$ was thereby decreased (compare Tables I and II).

The most notable effect of the scavenger was to eliminate the maximum in $b_{\rm GP}d$ (Fig. 2). Only a trace of the maximum remained in the presence of 0.1 mol % of SF_6. In the gas phase SF_6 has a large attachment cross section for electrons of energies less than 0.1 eV, and a smaller attachment peak at 0.3 eV.[32] Thus the peak in $b_{\rm GP}d$ can be mainly attributed to electrons with ~ 0.1 eV energy in the conduction band. In pure isobutane the value of $b_{\rm GP}$ for full thermalization at ~ 395 K is 25 nm (Table I). When the SF_6 concentration is 3.3×10^{24} molecules/m^3 the Wigner-Seitz distance between scavenger molecules is 8.3 nm, and the value of $b_{\rm GP}$ is reduced to 14 nm (Table II). The fact that 0.1 mol % of SF_6 can cause this large effect indicates that in pure isobutane at 395 K the mean energy loss per "collision" for ~ 0.1 eV electrons is $\sim 10^{-4}$ eV.

Eightfold increases of SF_6 concentration to 0.8 and 6 mol % decreased $b_{\rm GP}$ at 395 K to 12 and 8 nm, respectively (interpolated from Table II). Higher concentrations of the scavenger have relatively smaller effects, partly because higher energy electrons are less efficiently scavenged by SF_6.[32]

The Onsager model of free-ion formation has been modified to provide an approximate description of the effect of scavenging hot electrons.[13] It is a random-walk model that considers the probability that the epithermal electron will be captured as it moves along its bent path, and the distance of the newly formed negative ion from the cation. The assumed mechanism generates an initial anion-cation distance distribution function of the form $F(y)=(y/b_E^2)\exp(-y/b_E)$, where the correlation length b_E is given by

$$b_E=(L/6N\sigma)^{1/2}\,, \tag{10}$$

where L is the mean free path for elastic scattering, N is the scavenger concentration and σ is an average value of the capture cross section of the scavenger for the slowing-down electrons. Although the exponential form of $F(y)$ is probably not accurate, it will serve to illustrate the nature of the scavenger effect on $G_{\rm fi}$.

The analytical parameter used in the model is γ,[13] the ratio of the Onsager length to the distribution correlation length

$$\gamma=r_c/b_E\,. \tag{11}$$

The ratio of the free-ion yield in the presence of scavenger to that in the absence of scavenger is

$$F(\gamma)=G_{\rm fi}^{0}(N)/G_{\rm fi}^{0}(0)$$

$$=\int_0^\infty x\exp\left[-\left[x+\frac{\gamma}{x}\right]\right]dx\,, \tag{12}$$

where $x=y/b_E$. Calculated values of $F(\gamma)$ are plotted against γ in Fig. 3 of Ref. 13.

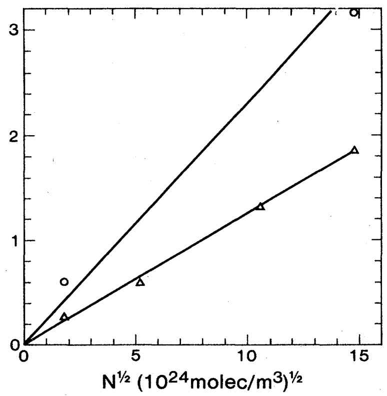

FIG. 3. Plot of the scavenging distribution parameter γ against $N^{1/2}$, where N = concentration of SF_6. ○, ~ 296 K; △, ~ 408 K.

The model is applied to the present results for ~ 296 K and ~ 408 K by (i) determining the experimental $F(\gamma)$ at each N; (ii) equating these values to γ's using the theoretical curves in Ref. 13 to generate a plot of γ vs $N^{1/2}$; (iii) drawing a line through the points; and (iv) calculating σ from the slope of the line. The plot of γ against $N^{1/2}$ is given in Fig. 3. The slope of the line equals $r_c(6\sigma/L)^{1/2}$, so σ/L is 8×10^{-12} m at 296 K and 2.5×10^{-12} m at 408 K. The value of L was previously taken as about a molecular diameter.[13] At 296 K, the Wigner-Seitz diameter for liquid isobutane is 7×10^{-10} m and at 408 K, 9×10^{-10} m. The use of these diameters as L gives $\sigma=6\times10^{-21}$ m^2 at 296 K and 2×10^{-21} m^2 at 408 K. These cross sections are similar to that reported for the dissociative capture of 0.37 eV electrons in the gas phase, 5×10^{-21} m^2.[32] They are 2 orders-of-magnitude smaller than the gas phase value for thermal (<0.1 eV) electrons.[33] The above model is very crude, but it offers support for the concept of the termination of hot-electron flight by the mechanism of electron capture.

D. Comments on photoionization and fluorescence mechanisms

The mechanisms of photoionization and of fluorescence of a solute such as TMPD (*N,N,N′,N′*-tetramethyl-*p*-phenylenediamine) in a liquid hydrocarbon are subjects of controversy.[34–36] The addition of an electron scavenger as an extra solute has no effect on the fluorescence yield when TMPD is excited below the ionization threshold.[34] However, when TMPD is excited to 1.2 eV above the ionization threshold an electron scavenger reduces the fluorescence yield and the ionization yield by similar amounts.[35(a)] The functional dependence of quenching on scavenger concentration is of the Stern-Volmer type, which seems to indicate that a quenchable Rydberg-like state of TMPD is the affected precursor of both ionization and fluorescence.[35(a)] By contrast, the electric field dependence of the ionization yield is altered by an electron scavenger in a manner that suggests that the affected precursor is the geminate ion-electron pair,[35(c)] and that electrons are scavenged before becoming thermalized. Our results are consistent with the latter interpretation.

Two further comments are worthwhile.

(1) It is not yet possible to experimentally distinguish between a metastable Rydberg-like state and a geminate ion-electron pair in the liquid phase. They could interact similarly with electron scavengers and with high electric fields. Arguments involving scattering probabilities indicate that in liquid hydrocarbons, other than perhaps methane, high Rydberg states have lifetimes less than 1 ps.[37]

(2) Solute molecules might reduce the flight distance of an electron away from the ion by two methods: (a) they might increase the scattering cross section of the fluid, thereby increasing the thermalization rate;[12] (b) they might capture electrons before thermalization is complete, thereby terminating the flight. Both processes are energy dependent. A simple exponential distribution of flight distances would only be produced by an energy independent process (b), so simple exponentials of the form $F(y) \propto y^n \exp(-y/b_E)$, with $n = 0$, 1, or 2, are not accurate for either photoionized or radiolyzed liquids.

E. Summary

The density-normalized thermalization distance $b_{GP}d$ in pure liquid isobutane has a maximum at $T = 395$ K$= T_c - 13$ K. The maximum is attributed to changes in scattering efficiency of epithermal electrons in the conduction band due to changes in the conduction band with density. Addition of small amounts of SF_6, an electron scavenger, removes the maximum by scavenging electrons in the conduction band at energies of ~ 0.1 eV.

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