Free-Ion Yield and Electron Mobility in Liquid Hydrocarbons: A Consistent Correlation

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A correlation is sought between the free-ion yield and electron mobility in liquid hydrocarbons in terms of the elastic and the inelastic scattering mean free paths of epithermal ($\leq$0.2 eV) electrons. *These determine the thermalization distance distribution and consequently the free-ion yield. The thermal quasi-free electron mobility,* μ_{qf}, *can also be obtained from the same cross sections. Finally, the effective mobility is derived from* μ_{qf} *using the electron trap concentration and binding energy, thereby establishing a relationship between free-ion yield and mobility. Thus, given the input data for trapping and the elastic and inelastic cross sections, both the free-ion yield and the effective mobility may be obtained from the interactions of epithermal electrons.* In very low mobility liquids ($\mu < 0.1$ cm^2 v^{-1} s^{-1}), transport is governed by trapping and detrapping rates, being relatively independent of μ_{qf}. As found by Jay-Gerin et al. (*Can. J. Chem.* **1993** , *71*, 287) the free-ion yield in such cases is virtually independent of mobility, a phenomenon which is naturally explained in the quasiballistic model of the author (*Chem. Phys. Lett*. **1993**, *207*, 245 and **1995**, *233*, 167) but not in the usual trapping model. For low mobility liquids, the elastic mean free path, *L*, is found to be ca. 1−5 A and there is a probability of ∼0.1−0.3 inelastic scatterings per elastic mean free path. These values increase progressively with mobility, where, in the high mobility cases, *L* is on the order of a few tens of angstroms and inelastic collisions outnumber elastic ones by a factor of ∼2−4. The situation is reminiscent of liquefied rare gases.

I. Introduction and Background

Ever since the early experimental measurements of the free-ion yield (G_{fi}) and electron mobility (μ) in liquid hydrocarbons, a correlation between these quantities was noticed. At present, various compilations of measured values are available,[1−4] and a systematization has been provided by Jay-Gerin et al.[5] In general, the free-ion yield at zero external field increases with electron mobility for many liquids in which the electron mobility ranges from ∼0.1 to ∼100 cm^2 v^{-1} s^{-1}, although deviations from the general rule can sometimes be seen.[6,7] The analysis of Jay-Gerin et al.[5] shows that at a very low electron mobility (<0.1 cm^2 v^{-1} s^{-1}), G_{fi}, the free-ion yield per 100 eV of deposited energy, remains essentially constant at ∼0.1, whereas at higher mobilities, it correlates with the mobility approximately by a power law of index 0.31. It will be shown that this finding has important consequences for the model of electron transport.

Onsager's[8] theory of geminate recombination is the most frequently used theoretical framework for the discussion of free-ion yield in terms of the initial electron−cation separation distance at thermalization. According to this theory, strictly applicable to isolated ion pairs, the free-ion yield is given by

$$G_{fi} = G_{tot} \exp(-r_c/r) \tag{1}$$

where G_{tot} is the total ionization yield, r is the initial or thermalization separation of the ion pair, and $r_c = e^2/\epsilon k_B T$, called the Onsager length, is the separation at which the ion pair potential is numerically equal to the thermal energy k_BT. Here e is the electronic charge, ϵ is the medium dielectric constant, k_B is the Boltzmann constant, and T is the absolute temperature. Often eq 1 is averaged over an assumed distribution of the thermalization distance. The distribution involves one or two adjustable parameters for comparison with experiment. However, since eq 1 is free of mobility, the relationship of the mobility with the free-ion yield has to be indirect, that is, via some common physical parameter that influences both of these in a like manner. An early attempt in this direction was made by Hentz [9] in terms of the electron scattering mean free path determining both the thermalization distance distribution and the mobility. However, due to the inadequacy of a suitable transport or trapping model, this line of reasoning was not pursued.

Of the various factors relating free-ion yield and mobility, the most frequently invoked is molecular sphericity.[10−15] The sphericity effect on mobility has also been seen in mixtures and in D-substituted liquid methanes.[16,17] However, it has been pointed out that the sphericity effect is a property of the liquid phase and not inherent in the molecular shape. For example, there is a reversal effect of sphericity on electron mobility between the gas and liquid phases, at least in some cases.[18] Allen's[2] conjecture that monatomic liquids and those polyatomics having molecules of nearly spherical symmetry provide the most regularly varying potentials for scattering gives a qualitative understanding why the electron mobility should be extraordinarily large in those liquids. However, it has proven to be very difficult to establish a quantitative basis for this idea. Other factors invoked to connect mobility and free-ion yield include the presence of π bonds in the molecule[19] and the anisotropy of molecular polarizability,[20−22] both of which are seen to reduce the mobility and the free-ion yield. Apart from observed correlation, however, these factors have not yielded any quantitative explanation.

On the theoretical side, the model of Schiller and Vass[23] attempts to connect the free-ion yield and mobility through the probability (P) of electron trapping, the electron energy in the trap, and the quasi-free mobility μ_{qf}. The electron trapping

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probability in turn is given in terms of the equilibrium fluctuation of the potential seen by the itinerant electron. Electron escape is seen as a combination (product) of two uncorrelated processes. The probability for escape to produce a quasi-free electron is assigned the value $\sim 1/2$ by a heuristic argument, which is not altogether clear. For the trapped electron, they apply the Onsager equation (see eq 1), averaged over an initial electron−cation distribution of separation given by an exponential function that involves the trapping cross section, the trap volume, and the probability of trapping. Thus, the free-ion yield is obtained from an assumed G_{tot} and the overall escape probability, while the effective mobility is given by $(1 - P)\mu_{\mathrm{qf}}$. Best agreement is obtained with $\mu_{\mathrm{qf}} = 65$ cm^2 v^{-1} s^{-1}, which falls short of the measured Hall mobility and drift mobility in some cases.[24] Agreement with experiments is none too good in the sense that G_{fi} remains nearly flat for a considerable range of values of the mobility. An earlier attempt by Funabashi and Kajiwara[25] was based on the resonance scattering formalism of epithermal electrons. Part of the scattering was envisaged as due to the traps themselves. Traps originate from preexisting potential related to fluctuation of polarization and transfer energies; the latter is defined by the authors as the resonant energy between nearest neighbor molecules when the electron is transferred between them.[25] Shallower potentials result from more spherical molecules. Although an exponential distribution of thermalized electron−cation separation was derived in this model consistent with a class of experiments on scavenging and on the effect of an external electric field on the free-ion yield, apparently no attempt was made to calculate the free-ion yield or mobility. Another theoretical model of Sano and Mozumder[26] is based on the energy loss of epithermal electrons in the Fokker−Planck formalism. However, this model does not consider trapping and therefore it is limited to high mobility cases only.

In this paper a theoretical model is presented in which a representative thermalization distance is calculated starting with a subvibrational energy[27,28] and using appropriate elastic and inelastic mean free paths. Loss of kinetic energy of the epithermal electron due both to intermolecular interaction and to work against the attraction of the cation are considered. Thus, the thermalization distance in the Coulombic field is determined. Simultaneously, the momentum relaxation time of the epithermal electron, and therefore the epithermal mobility, is obtained from the scattering mean free path and velocity. From the epithermal mobility, the thermal quasi-free electron mobility is evaluated by velocity scaling according to the Lorentz model. Finally, the effective mobility is computed in a two-state trapping theory using a quasi-ballistic model developed by the author.[29,30] The observation that the free-ion yield remains essentially independent of effective mobility in very low mobility cases[5] finds a natural explanation in the quasi-ballistic model (vide infra), but it cannot be understood in the usual trapping model. In section II we develop the theoretical model in some detail showing the relationship of the elastic and the quasi-inelastic mean free paths with a typical *thermalization distance in the Coulombic field*, thereby bringing a connection between the free-ion yield and mobility. In section III, we compute and compare with experiments the results obtained for three classes of liquids having low, intermediate, and high measured mobilities. In each case, we get the mean free path of elastic scattering of epithermal electrons and a probability (or mean free path) of inelastic scattering per elastic interaction. Finally, we summarize our findings and conclusions in section IV.

II. Theoretical Model

Scattering Mean Free Paths, Thermalization Distance, and Free-ion Yield. Consider, as in refs 27 and 28, an electron degraded to subvibrational kinetic energy, E_0, at a distance, R_0, from its geminate positive ion. If r_{th} is a representative thermalization distance[31] for that electron, then the loss of kinetic energy during the thermalization process is $E_0 - (3/2)k_{\mathrm{B}}T$. Part of the kinetic energy loss is due to working against the Coulombic attraction and the rest due to irreversible inelastic encounters. The first part equals the difference between the potential energies at the initial and final positions and it is given by $(e^2/\epsilon R_0)(1 - \mathrm{R}_0/r_{\mathrm{th}})$. Therefore, the overall energy loss due to inelastic encounters only would be given by

$$(E_0 - 3k_{\mathrm{B}}T/2) - (e^2/\epsilon R_0)(1 - R_0/r_{\mathrm{th}}) \qquad (2)$$

Proper thermalization of epithermal electrons requires both energy loss and gain by inelastic encounters so that equilibrium may be established in the long time limit. When the inelastic interaction is modeled by the exchange of a single quantum of energy $\hbar\omega$ at epithermal electron energy E, then the ratio of the numbers of energy-gaining collisions to energy-losing collisions is given by[28]

$$n_{\mathrm{g}}/n_{\mathrm{l}} = (1 - \hbar\omega/E)^{-1} \exp(-\hbar\omega/k_{\mathrm{B}}T) \qquad (3)$$

Since the overall number of energy-losing collisions $(n_{\mathrm{l}} - n_{\mathrm{g}})$ must be given by expression 2 divided by $\hbar\omega$, one gets n_{l} and n_{g} from eqs 2 and 3 with which the total number of inelastic collisions during thermalization, $n_{\mathrm{in}} = (n_{\mathrm{l}} + n_{\mathrm{g}})$, may be given as follows:

$$n_{\mathrm{in}} = \left[\frac{(1 - \hbar\omega/E) + \exp(-\hbar\omega/k_{\mathrm{B}}T)}{(1 - \hbar\omega/E) - \exp(-\hbar\omega/k_{\mathrm{B}}T)}\right](\hbar\omega)^{-1}[(E_0 - 3k_{\mathrm{B}}T/2) - (e^2/\epsilon R_0)(1 - R_0/r_{\mathrm{th}})] \qquad (4)$$

If k denotes the ratio of the number of inelastic to elastic collisions (the reciprocal of the respective mean free paths), then during thermalization the number of elastic collisions would be given by $n_{\mathrm{el}} = n_{\mathrm{in}}/k$. On the random walk model $r_{\mathrm{th}}{}^2 = n_{\mathrm{el}}L^2$, where L is the mean free path of elastic collisions. Therefore we obtain from eq 4

$$r_{\mathrm{th}}{}^2 = \left(\frac{L^2}{\mathrm{k}}\right)\left[\frac{(1 - \hbar\omega/E) + \exp(-\hbar\omega/k_{\mathrm{B}}T)}{(1 - \hbar\omega/E) - \exp(-\hbar\omega/k_{\mathrm{B}}T)}\right](\hbar\omega)^{-1}\left[\left(E_0 - \frac{3}{2}k_{\mathrm{B}}T\right) - \frac{e^2}{\epsilon R_0}(1 - R_0/r_{\mathrm{th}})\right] \qquad (5)$$

Equation 5 may be considered an implicit equation for r_{th}. Alternatively, if r_{th} is known from some other consideration (e.g., from the free-ion yield), then eq 5 can be used to evaluate L and k. To obtain r_{th} from the free-ion yield (cf. eq 1), one needs an estimate of the total ionization yield, which in many liquid hydrocarbons has been found from scavenging studies to be $G_{\mathrm{tot}} \sim 4$. In this paper, a uniform value of 4.3 has been used in all liquids. In any case, both procedures serve as a consistency check on the values of physical parameters. With known values of L and k, the electron mobility can be calculated in the relaxation time formalism as shown in the next paragraph.

Epithermal, Quasi-Free, and Effective Mobilities. In the relaxation time formalism, the mobility may be generally written as $\mu = (e/m)\tau$, where the relaxation time, $\tau = \tau(v)$, is a function of electron velocity or energy. For a low-mobility liquid, such as *n*-hexane, the full momentum relaxation of an epithermal electron (~0.2 eV energy, taken as a midpoint between E_0 and thermal energy) would require about one effective energy loss collision (i.e., loss-gain). *At this stage in the development of our theory, this is a hypothesis*. The total number of inelastic collisions for one effective energy loss collision is given by the procedure in the previous paragraph as $[(1 - \hbar\omega/E) + \exp(-\hbar\omega/k_BT)]/[(1 - \hbar\omega/E) - \exp(-\hbar\omega/k_BT)]$. With inelastic to elastic collisions divided in the ratio of k:1, the corresponding number of elastic collisions during this process is given as follows:

$$(k^{-1})[(1 - \hbar\omega/E) + \exp(-\hbar\omega/k_BT)]/[(1 - \hbar\omega/E) - \exp(-\hbar\omega/k_BT)] \quad (6)$$

Denoting by v_{epi} (2.7×10^7 cm/s) the electron velocity at typical epithermal energy ~0.2 eV and using the Lorentz approximation of independence of elastic scattering mean free path on velocity, the epithermal relaxation time is obtained from expression 6 as

$$\tau_{epi} = \left(\frac{L}{kv_{epi}}\right)\left[\frac{(1 - \hbar\omega/E_{epi}) + \exp(-\hbar\omega/k_BT)}{(1 - \hbar\omega/E_{epi}) - \exp(-\hbar\omega/k_BT)}\right] \quad (7)$$

where E_{epi} is a typical epithermal energy (taken here as 0.2 eV). The epithermal electron mobility is now obtained from eq 7 as follows:

$$\mu_{epi} = (e/m)\tau_{epi} \quad (8)$$

Assuming that thermalization precedes trapping, the quasi-free thermal electron mobility is given on the Lorentz model as

$$\mu_{qf} = \mu_{epi}(v_{epi}/v_{th}) = 2.31(e/m)\tau_{epi} \quad (9)$$

where $v_{epi} = 1.17 \times 10^7$ cm/s is the thermal electron velocity at 300 K and τ_{epi} is given in eq 7. Deriving the effective electron mobility, to be consistent with experiment, from the quasi-free mobility requires the rates of trapping (k_{ft}) and detrapping (k_{tf}), which in turn are obtainable from the trap depth and trap density on a certain model.[29] In the present context, *effective mobility* means calculated thermal electron mobility in the presence of trapping, which is to be finally compared with experimental determination. Often the effective mobility is numerically equated to the experimental value to obtain data on trap concentration, trap depth, etc. In the usual two-state trapping model, the effective mobility is given by $\langle\mu\rangle_F = \mu_{qf}\tau_f/(\tau_t + \tau_f)$ while in the quasi-ballistic model of the author the same is given as follows:

$$\mu_{eff}^{-1} = \langle\mu\rangle_T^{-1} + \langle\mu\rangle_F^{-1}; \qquad \langle\mu\rangle_T = (e/m)\tau_f^{2}/(\tau_t + \tau_f) \quad (10)$$

In eq 10, $\tau_f \equiv k_{ft}^{-1}$ and $\tau_t \equiv k_{tf}^{-1}$ are respectively the mean time spent by the electron in the quasifree and trapped states, respectively, and $\langle\mu\rangle_T$, called the ballistic mobility,[29] refers to electron transport only by random trapping and detrapping irrespective of the quasi-free mobility. *In the present scheme, the free-ion yield is related to the effective mobility by the scattering mean free path L via the trapping and detrapping rates*. However, it has been shown[29,30] that in very low-mobility hydrocarbon liquids the ballistic mobility dominates transport, which gradually shifts to the usual trap-controlled mobility as the effective mobility increases. This phenomenon explains why the free-ion yield is relatively insensitive to the effective mobility in very low-mobility liquids (see section III below).

III. Results and Discussion

The experimental data on the free-ion yield, dielectric constant, and mobility are taken from Jay-Gerin et al.[5] In some cases, as indicated, the data are culled from the compilations of Allen.[1,2] Therefore, the r_{th} values used in this paper are the same as those of b,[5] which is the most probable thermalization distance appropriate for an implied distribution. In some cases, r_{th} has been obtained from the free-ion yield using eq 1 and taking the total ionization yield as 4.3. Values of R_0, E_0, and $\hbar\omega$ are taken to be the same as in *n*-hexane, i.e., 23 Å, 0.4 eV, and 0.01 eV, respectively,[28] as no great variation of these values are expected among liquid hydrocarbons. The general procedure has been to derive a pair of values of L and k that would be consistent with the free-ion yield and electron mobility in a given liquid. First, we discuss the special cases of *n*-hexane, tetramethylsilane (TMS), and neopentane. Then the classes of low and intermediate mobility liquids will be considered as separate groups.

***n*-Hexane**. This liquid is a paradigm for low electron mobility and for a small probability of free-ion formation. It has been investigated extensively for free-ion yield, mobility, and the effects of external field on these. In it $k = 0.325$ and L ~ 5 Å were found by a detailed Monte Carlo study of thermalization and comparison with experimental free-ion yield.[28] Taking $T = 300$ K, we obtain from eqs 7−9 $\tau_{epi} = 3.3 \times 10^{-14}$ s, $\mu_{epi} = 58$ cm^2 v^{-1} s^{-1}, and $\mu_{qf} = 134$ cm^2 v^{-1} s^{-1}, respectively. This value of the quasi-free mobility is somewhat larger than 100 cm^2 v^{-1} s^{-1}, which is often assumed for liquid hydrocarbons,[30,32,33] but it is not unreasonable. Previous calculation[30] on the quasi-ballistic model using $\mu_{qf} = 100$ cm^2 v^{-1} s^{-1}, $n_t = 1.0 \times 10^{19}$ cm^{-3}, and ϵ_0(trap depth) = 0.15 eV reproduced the experimental mobility at 300 K of $\mu_{eff} = 0.1$ cm^2 v^{-1} s^{-1} with $\langle\mu\rangle_T = 0.170$ cm^2 v^{-1} s^{-1} and $\langle\mu\rangle_F = 0.295$ cm^2 v^{-1} s^{-1}. With the new value of $\mu_{qf} = 134$ cm^2 v^{-1} s^{-1}, the same experimental mobility can be matched for a slightly modified value of the trap density $n_t = 1.1 \times 10^{19}$ cm^{-3} while other parameters remain fixed. It also shows that the ballistic mobility dominates for this low-mobility liquid.

Tetramethylsilane (TMS). This liquid is considered essentially free of electron traps, as the activation energy for mobility is ~0[2] and the Hall mobility nearly equals the drift mobility.[24] Further, the measured drift mobility,[34] ~100 cm^2 v^{-1} s^{-1}, is consistent with the quasi-free mobility. Therefore, equating the measured drift mobility with the quasi-free mobility we get from eq 9 $\mu_{epi} = (v_{th}/v_{epi})\mu_{qf} = 43$ cm^2 v^{-1} s^{-1} and $\tau_{epi} = 2.45 \times 10^{-14}$ s. *Now the factor within the square brackets on the right-hand side of eq 7 remains essentially constant in all cases at 5.79 for the parametric values used in this paper*. For TMS, we then get $(L/k) = \tau_{epi}v_{epi}/5.79 = 1.14 \times 10^{-7}$ cm. In TMS the thermalization distance $r_{th} = b$ is 160 A.[5] Substituting this in eq 5 and using the standard parametric values at 300 K we obtain $L^2/k = 5.31 \times 10^{-14}$ cm^2. Combining our estimates of L/k and L^2/k, we get $L = 46.7$ Å and $k = 4.1$ in TMS at $T = 300$ K. That is, per elastic collision, there are ca. four inelastic collisions. The result, although not as extreme, may be interpreted as in liquid argon;[35] i.e., large angular deviation contributing to diffusion results from elastic collision while inelastic collisions give small angular scattering. The situation is exactly opposite to that in *n*-hexane.

Neopentane (NP). Although the measured room-temperature mobility in this liquid is quite high ~70 cm^2 v^{-1} s^{-1}, there is

TABLE 1: Parameters of the Quasi-Ballistic Model for Low-Mobility Liquids[a]

liquid	ϵ_0[b]	n_t[c]	$\langle\mu\rangle_T$[d]	$\langle\mu\rangle_F$[e]	μ_{eff}[f,g]
toluene	0.17	0.75	0.120	0.180	0.072
m-xylene	0.17	0.80	0.106	0.166	0.065
n-octane	0.17	1.0	0.068	0.133	0.040
trans-but-2-ene	0.17	1.2	0.047	0.111	0.033
1,2,3,4-tetramethylbenzene	0.17	1.5	0.030	0.088	0.022

[a] All mobilities are in cm^2 v^{-1}s^{-1} at $T = 300$ K and with $\mu_{qf} = 100$ cm^2 v^{-1} s^{-1}. [b] Trap depth (eV). [c] Trap concentration in 10^{19} cm^{-3}. [d] Ballistic mobility. [e] Trap-controlled mobility. [f] Effective mobility. [g] Experimental values, to which the computed μ_{eff} are numerically equated, are subject to uncertainties. There are also variations from one laboratory to another. The numerical values quoted here are close to literature values as best-judged.

evidence of electron trapping. The activation energy for mobility, 0.014 eV,[2] is positive and the Hall mobility significantly exceeds the drift mobility over a wide range of temperature.[24] On the quasi-ballistic model[30] we get a match for the measured drift mobility and its activation energy at 300 K with $\mu_{qf} = 215$ cm^2 v^{-1} s^{-1} and $n_t = 1.0 \times 10^{19}$ cm^{-3}, implying $\langle\mu\rangle_T = 307$ and $\langle\mu\rangle_F = 91$ cm^2 v^{-1} s^{-1}, respectively. Notice that in NP the transport is dominated by ordinary trap-controlled motion and not by ballistic trapping and detrapping. This is characteristic of high mobility liquids. Further, the high value of the measured mobility necessitates a higher quasi-free mobility. Proceeding as in the case of TMS, we get from eq 9 $\mu_{epi} = 93.2$ cm^2 v^{-1} s^{-1} and $\tau_{epi} = 5.3 \times 10^{-14}$ s, which gives from eq 7, $L/k = 2.47 \times 10^{-7}$ cm. The thermalization distance parameter ($r_{th} = b$) in NP is 217 Å.[5] Using this value and standard parametric values in eq 5, we get $L^2/k = 1.69 \times 10^{-13}$ cm^2. On combination we then obtain $L = 68$ A and $k = 2.78$ in NP at 300 K. The interpretation is similar as in TMS; i.e, there are ca. three inelastic collisions per large angle elastic collision.

Low-Mobility Liquids. We consider five liquids in this group in which the measured electron mobility is <0.1 cm^2 v^{-1} s^{-1}; the result of an analysis on the quasiballistic model[30] is shown in Table 1. For these liquids the quasi-free mobility may be taken to be sensibly constant at 100 cm^2 v^{-1} s^{-1}. Since the trap depth (ϵ_0) is also constant at 0.17 eV in these liquids, the variation of the effective mobility is attributable to trap concentration. *Note that ballistic mobility is dominant in this group.*

Since G_{fi} is nearly constant in this group, the thermalization distance parameter is also nearly so, with minor variation due to the dielectric constant.[5] However, in actual calculation, the respective values of b and ϵ given in ref 5 have been used. Taking a constant $\mu_{qf} = 100$ cm^2 v^{-1} s^{-1} for this group, values of the epithermal mobility and epithermal relaxation time also remain constant with $\tau_{epi} = 2.46 \times 10^{-14}$ s (cf. the case of *n*-hexane and note that the mobility is proportional to the relaxation time). Therefore, from eq 7, we get for all liquids in this group $L/k = 1.15 \times 10^{-7}$ cm. Equating the thermalization distance parameter r_{th} with b of ref 5 and using the fixed parametric values of this paper, eq 5 may be rewritten as

$$L^2/k = 10^{-18} x b^2(\text{Å})[2.10 - (3.63/\epsilon)(1.0 - 23.0/b(\text{Å}))]^{-1} \tag{11}$$

Using eq 11 and the fixed value of L/k for this group, we get the specific values of L and k for the individual liquids that are collected in Table 2 along with the values of G_{fi}, b, and ϵ from ref 5. Generally, L increases with k. It is understood that to obtain similar thermalization distance, a longer elastic mean free path has to be associated with a greater probability of inelastic scattering.

TABLE 2: Free-ion Yield, Scattering Mean Free Path and Probability of Inelastic Collision for Low-mobility Liquids

liquid	G_{fi}[a]	b (Å)[b]	ϵ[c]	L (Å) [d]	k[e]
toluene	0.09	43	2.38	1.15	0.10
m-xylene	0.08	41	2.37	1.04	0.09
n-octane	0.13	58	1.95	2.91	0.25
trans-but-ene	0.08	53	1.84	2.55	0.22
1,2,3,4-tetramethylbenzene	0.11	42	2.54	1.06	0.09

[a] Free-ion yield per 100 eV of deposited energy at ~300 K. [b] Thermalization distance parameter from ref 5. [c] Dielectric constant from ref 5. [d] Elastic mean free path from this work. [e] Ratio of inelastic to elastic cross sections from this work.

TABLE 3: Free-ion Yield and Mobility Data for Intermediate and High Mobility Liquids[a]

liquid	G_{fi}[b]	μ_{eff}[c]	ϵ[d]	ϵ_{ac}[e]	b (Å)[f]
3-methylpentane	0.18	0.2	1.90	0.20	67
cyclohexane	0.20	0.45	2.02	0.13	59
isooctane	0.35	4.5	1.94	0.05	110
2,3-dimethylbut-2-ene	0.44	6.0	1.98	0.055[g]	102
isobutane	0.51	7.3	1.74	0.055[g]	116
neohexane	0.58	12.0	1.87	0.06	120
tetramethyltin	0.63	78.0	2.25	0.014[h]	115
tetramethylgermanium	0.66	90.0	2.01	0.014[h]	143

[a] Experimental data on free-ion yield and mobility, to which our calculated values are nominally equated, are literature based. Since experimental determinations have inherent uncertainties and variations from one laboratory to another, there are no unique, precise values. Those reported here are taken from literature as best-judged. [b] Free-ion yield per 100 eV at ~300 K. [c] Effective mobility at ~300 K (cm^2 v^{-1} s^{-1}). [d] Dielectric constant. [e] Activation energy of mobility (eV). [f] Thermalization distance parameter (ref 5). [g] Assumed. [h] Assumed to be the same as in neopentane.

The principal result for the low-mobility liquids is that the elastic mean free path (L) and the ratio of inelastic to elastic collisions (k) are quite comparable (i.e., within a factor of 3 or so) in different liquids. This gives rise to comparable thermalization lengths and free-ion yields. Consequently, the quasi-free mobilities are also the same. The trap-controlled mobility $\langle\mu\rangle_F$ varies only within a factor of about 2 (see Table 1). However, for these liquids, the ballistic mobility dominates, which is determined by the rates of trapping and detrapping independently of the quasi-free mobility. Therefore, as seen from Tables 1 and 2, the effective mobility is not correlated with L or k, which is the underlying reason the observed mobility is relatively independent of the free-ion yield for low-mobility liquids.[5]

Intermediate and High Mobility Liquids. We consider eight liquids in this group in which the observed mobility is >0.1 cm^2 v^{-1} s^{-1}. As seen in Table 3, these liquids may be subdivided into two groups in two different ways. One way is based on whether μ_{eff} is less than or greater than 10 cm^2 v^{-1} s^{-1}; accordingly, the first five liquids fall in the first subgroup. Another way is based on whether the b-value is small (~60 Å) or large (ca. 100−140 Å). By this criterion the first two liquids, along with *n*-hexane, fall in the first subgroup; the rest in the second. In every case eq 11 still remains valid and L^2/k can be determined from known values of b and ϵ. As for L/k, we notice, as remarked earlier, that the factor within the square brackets on the right-hand side of eq 7 remains fixed at 5.79 for all liquids with same values of input parameters. Then, by successive elimination, one gets from eqs 7−9 $L/k(\text{cm}) = 1.15 \times 10^{-9}\mu_{qf}(\text{cm}^2\ \text{v}^{-1}\ \text{s}^{-1})$. Combining this with eq 11 gives the values of L and k in each liquid. Figure 1 shows L, k, and G_{fi} for these liquids as functions of the effective mobility. It is apparent that for liquids in this group the free-ion yield increases

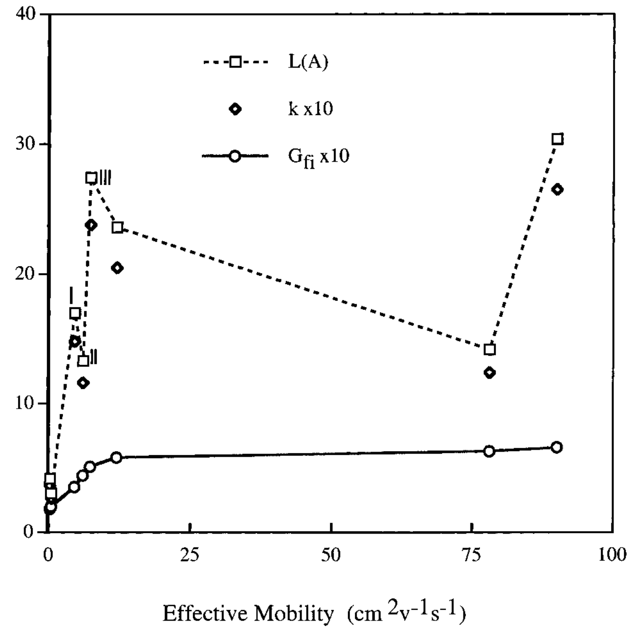

Figure 1. Free-ion yield (G_{fi} × 10), elastic scattering mean free path [L (Å)], and ratio of inelastic to elastic scattering cross-section (k × 10) plotted as functions of effective mobility. Isooctane, 2,3-dimethylbut-2-ene, and isobutane are indicated by I, II, and III, respectively. See the text for details.

systematically with the effective mobility; however, the increase is more significant in the lower mobility range. For high mobility liquids, the transport is dominated by the trap-controlled mobility $\langle\mu\rangle_F$. For the intermediate mobility liquids, $\langle\mu\rangle_F$ still makes a significant contribution. Therefore, both the free-ion yield and the effective mobility are governed by the same L and k, resulting in a correlation. As seen in Figure 1, L and consequently k increase in overall with the effective mobility. Some local variation is nevertheless observed, which may be rationalized with other factors in the quasiballistic mobility theory.

Some comments may be made for tetramethyltin and tetramethylgermanium, in which the measured mobility is very high but the activation energy (E_a) is not known. We assume an activation energy similar to NP, i.e., ~0.014 eV, and we utilize a relationship with the binding energy in the trap found for many liquids using the quasi-ballistic model,[30] viz. $\epsilon_0/E_a = 0.885$. As in the case of NP, we have assumed the electron trap density in these liquids to be 1.0×10^{19} cm^{-3}. Adopting these values, the best agreement for the observed mobility (see Table 3) is obtained with a quasi-free mobility of 225 and 300 cm^2 v^{-1} s^{-1}, respectively, for these liquids. The rest of the calculation proceeds as for NP.

From Figure 1 we see that, in some cases, as for instance, isooctane, 2,3-dimethylbut-2-ene, and isobutane, the elastic and inelastic cross sections (values of L, k) are comparable and that the momentum transfer cross-section is smaller than geometric. For isooctane, we prefer μ_{qf} = 100 cm^2 v^{-1} s^{-1} [30] to the experimental value of the Hall mobility 22 cm^2 v^{-1} s^{-1}.[36] If we use the experimental value of the Hall mobility for the quasi-free mobility, then we get L = 78 Å and k = 31; both of these values seem unreasonable to us. Sometimes there could be a difference between Hall and quasi-free mobilities[37,38] for reasons outside the scope of the present paper.

IV. Summary and Conclusions

The same elastic and inelastic processes are involved in the thermalization of a subvibrational electron in a hydrocarbon liquid as in its transport in the quasi-free state. When the effective mobility is simply related to the quasi-free mobility, as in liquids of intermediate and high electron mobility, the free-ion yield is directly correlated with the mobility via the thermalization distance. On the other hand, in liquids of low electron mobility, the transport is often dominated by the ballistic motion caused by just random trapping and detrapping irrespective of the quasi-free mobility. In the quasi-ballistic model of transport recently developed by the author[29,30] the effective mobility is *not directly* related to the quasi-free mobility, and so the free-ion yield remains nearly the same so long as the effective mobility remains low. This feature, which has been experimentally verified,[5] cannot however be explained with the usual trapping model.

In low and intermediate mobility liquids, the quasi-free mobility is about 100 cm^2 v^{-1}s^{-1}. The elastic scattering mean free path, which is on the order of a few angstroms, is small, and inelastic collisions are relatively infrequent. In some high mobility liquids, the quasi-free mobility increases by a factor of 2−3, the elastic scattering mean free path, which is on the order of a few tens of angstroms, is large, and the inelastic collisions are relatively frequent. The transport is qualitatively similar to that in liquefied rare gases, although not so severe.

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