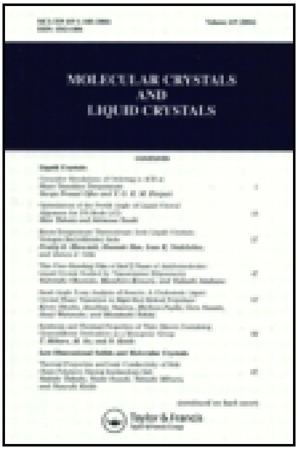

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A Current Look at Electron Transport in Organic Liquids

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A Current Look at Electron Transport in Organic Liquids

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Recent measurements of the drift mobility (μ_D) of electrons in hydrocarbon liquids at high pressure and of the Hall mobility (μ_H) as a function of temperature are discussed. In some highly branched alkanes $\mu_H \simeq \mu_D$; also high pressure causes μ_D to increase at 20°C. These facts are consistent with the tenet that in these liquids electrons remain quasi-free, the observed mobility being a result of scattering due in large part to density fluctuations. For normal and singly branched alkanes the mobility is determined by an equilibrium distribution of electrons between the trapped and quasi-free states. High pressure shifts this equilibrium toward the trapped state because of a volume decrease occurring on trapping. This volume change is attributed to electrostriction of the solvent by the trapped electron.

INTRODUCTION

Recent studies of excess electrons in non-polar liquids have provided new insight into the transport mechanism. In this paper measurements of a) the drift mobility at pressures up to 3000 atmospheres and b) the Hall mobility as a function of temperature, are discussed. First, in order to put these studies in perspective some other significant experimental results as well as theoretical models are reviewed briefly. Past studies have established that the mobility of excess electrons in alkanes depends on many factors. Some important ones are: molecular symmetry, temperature, density, conduction band energy, phase, and compressibility. The role of these factors is illustrated in the following discussion.

TEMPERATURE EFFECTS

The effect of temperature on the electron drift mobility depends on whether the alkanes are branched (symmetrical) or linear (unsymmetrical). For example, the electron mobility in *n*-hexane from 190 to 300 K exhibits Arrhenius-like behavior, the activation energy is constant at 0.16 eV,[1] and the mobility at 20 C is low, 0.07 cm^2/Vs. For liquids like *n*-hexane which show temperature activated Arrhenius-like behavior, the two-state model is often invoked. This presumes that electrons are temporarily trapped; that is, localized at preexisting sites in the liquid. The localized electron is relatively immobile and transport occurs when it is activated to the quasi-free or extended state. Thus an equilibrium:

$$e_{qf} \rightleftarrows e_{tr}, \tag{1}$$

exists and the observed mobility depends on the mobility in the quasi-free state and the fraction of time the electron is in this state.

In contrast, for 2,2-dimethylbutane the mobility is less temperature sensitive. An Arrhenius plot of the mobility data is curved and around 200 K the activation energy is nearly zero.[2] Also, it is important to note that for symmetrical molecules the mobility is generally high, for 2,2-dimethylbutane it is 12 cm^2/Vs. The behavior of other branched alkanes like neopentane for example, is similar to that exhibited by 2,2-dimethylbutane. One tenet of this paper is that for these liquids the electron is at most times in the quasi-free state; its mobility changing with conditions only as a result of changes in the scattering cross section.

DENSITY EFFECTS

Measurements of electron mobility as a function of temperature are usually made along the liquid-vapor coexistence line. Thus the densities of the liquid and vapor are also changing as the temperature is changing. Such mobility data can alternatively be plotted as a function of density as is shown in Figure 1A.[2,3] For neopentane, as the density increases, the mobility first decreases, passes through a minimum near the critical density, then increases to a maximum at a density of 3.5×10^{21} cm^{-3} and finally decreases as the room temperature density of about 5×10^{21} cm^{-3} is approached. This behavior is typical of symmetrical alkanes and is also observed for methane as well as for argon, krypton, and xenon.[5] Also shown in the figure by the dashed line is data obtained at a constant temperature of 161 C, just above T_c.[3,4] The curves are nearly coincident suggesting that the important parameter affecting the mobility is the density.

The mobility in *n*-pentane, shown by the dotted line in Figure 1, is comparable to that in neopentane at low densities, but drops dramatically at densities greater than 3×10^{21} cm^{-3} and is only 0.13 cm^2/Vs at room temperature. This decrease is attributed, as in the case of *n*-hexane, to trapping of the electron at high densities/low temperature. Most normal, as well as singly branched alkanes, behave similarly. In this case the temperature is still an important parameter. That is, an increase in temperature shifts the equilibrium in equation 1 to the left.

Of relevance to this symposium are the results obtained in solid hydrocarbons. Here again the behavior of compounds composed of symmetrical molecules, where the electron is quasi-free, contrasts with that observed for compounds where the electron is trapped. For neopentane, methane, argon, krypton and xenon, the mobility increases by roughly a factor of two on freezing, as is shown in Table I.[6-8] The scattering cross section becomes significantly less in the solid. This is attributed to the fact that the compressibility of the solid is less than that of the liquid.

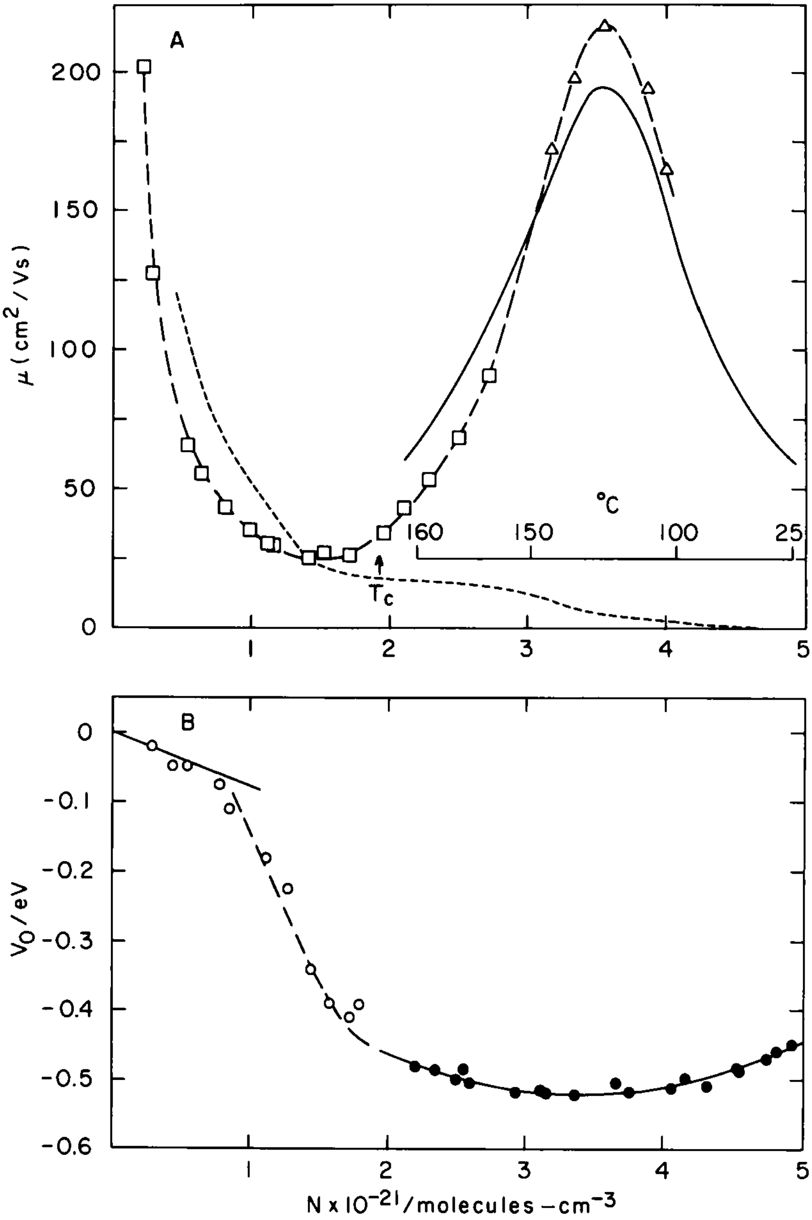

FIGURE 1 A—Electron mobility in neopentane vs density, liquid ———, reference 2; supercritical data at 161 C, □—reference 3, △—reference 4. Mobility in *n*-pentane --- reference 2. B—Conduction band energy (V_0) for neopentane vs density—reference 3.

Furthermore, in solid neopentane the mobility increases with decreasing temperature, following a $T^{-3/2}$ law, characteristic of acoustic-mode scattering.[7]

On the other hand, in liquids where the electron is trapped, cyclohexane and 2,2,4-trimethylpentane, for example, the mobility decreases on freezing. This is presumably due to the increased importance of trapping in the more dense (solid) phase.

DEFORMATION POTENTIAL MODEL

A discovery of significance to the theory of electron transport of quasi-free electrons was the observation that the energy of the bottom of the conduction band (denoted V_o) exhibits a minimum around the density at which the mobility is a maximum.[3] This correlation is shown in Figure 1 for neopentane. Similar correlations have been found for argon, krypton, xenon, methane and tetramethylsilane.[9-11]

The shape of the $V_o(N)$ curve and particularly the minimum is important in the deformation potential model of electron transport of quasi-free electrons.[12] This model assumes that the scattering arises from a potential produced by fluctuations in fluid density. The scattering cross section is a function of derivatives of V_o with respect to N: V_o', V_o'', etc. According to this theory the mobility can be written as:

$$\mu = (2e/3)(2/\pi \mathrm{m} kT)^{1/2}\, \Lambda \tag{2}$$

where Λ, the mean free path is given by:

$$\Lambda = \pi\hbar^4/m^2N^2kT\chi_T(V_o'^2 + V_o''^2\beta/kT\chi_T + \ldots) \tag{3}$$

The mobility thus depends on: m, the effective mass of the electron; N, the number density; χ_T, the isothermal compressibility; and the derivatives of V_o. At the min-

TABLE I

Drift Mobility Changes on Freezing

	Liquid		Solid	
	Temp K	μ^a cm^2/Vs	Temp K	μ^a cm^2/Vs
Argon	85	475	82	1000
Krypton	117	1800	113	3700
Xenon	163	2200	157	4500
Methane	98	530	87	1100
Neopentane	258	71	257	154[c]
2,2,4-Trimethylpentane	160	1.0	155	0.6[b]
Cyclohexane	283	0.15	273	0.06[b]

[a] Reference 6
[b] Reference 8
[c] Reference 7

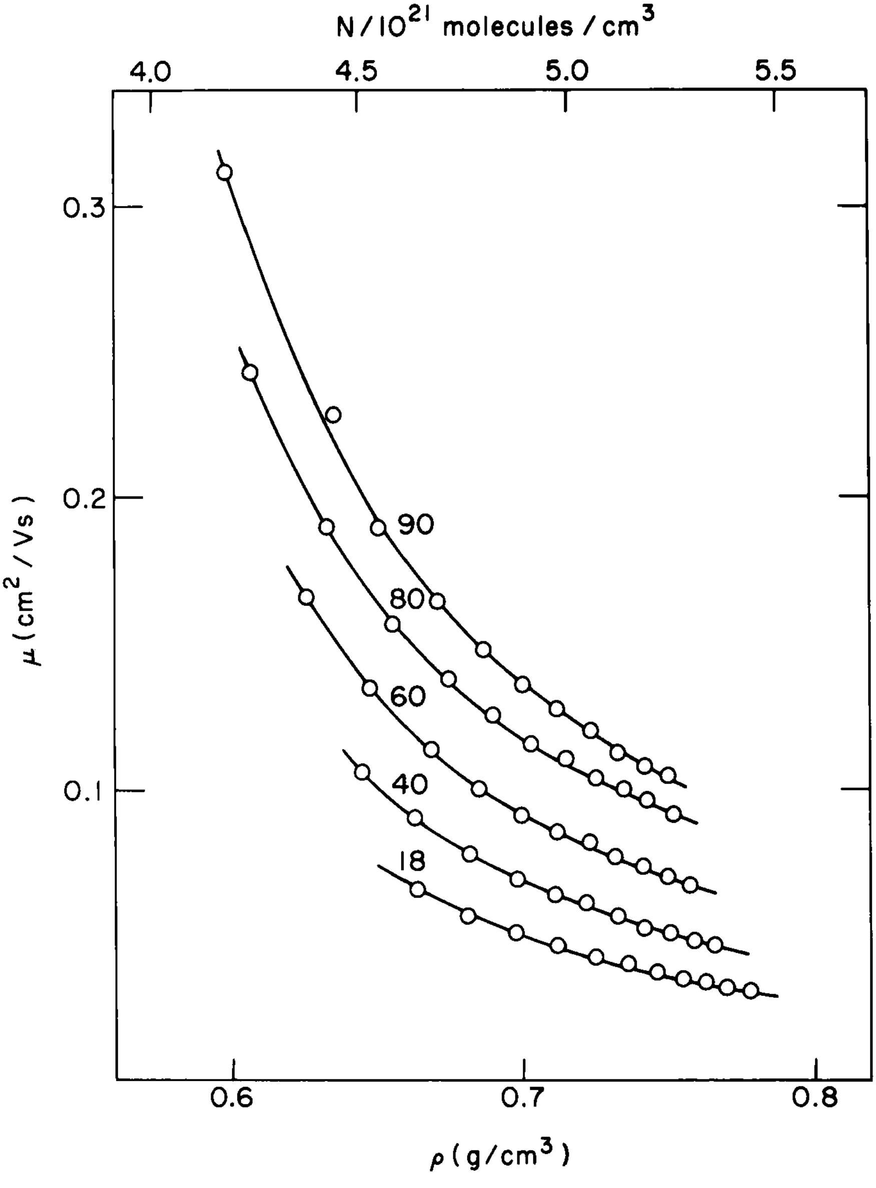

FIGURE 2 Electron mobility in *n*-hexane vs density for pressures between 1 and 2500 bar, Reference 15, temperature in °C indicated on Figure.

imum, the first derivative, V_o', is zero, thus the mobility should be a maximum near the same density. This theory is analogous to the deformation potential model for electron transport in solids. A modified version of the latter has been applied to the liquid rare gas fluids. In the case of xenon the calculated mobility is in excellent agreement with experiment.[13]

HIGH PRESSURE STUDIES

The mobility of excess electrons has recently been measured in several liquids under static pressures up to 3 kbar.[14-16] These studies were motivated by the lower density studies described above which stopped at the normal liquid density. Use of pressure allows measurements at higher density and permits independent variation of density and temperature. Volume changes can also be deduced from such studies and one goal was to determine the partial molar volume of the trapped electron. Another motive was to look for mobility transitions at higher densities. This is of particular interest because of the recent path integral calculations[17] which predict localization for hard sphere solvents as the density is increased.

For *n*-hexane, *n*-pentane and 3-methylpentane, in which the electron mobility is low at 1 atmosphere, pressure causes the mobility to decrease.[15,16] The results for *n*-hexane from 1 bar to 2.5 kbar are shown plotted vs density in Figure 2. At all temperatures the mobility decreases monotonically with increasing density. At any given density the mobility increases with increasing temperature; that is, Arrhenius-type behavior is observed. The interpretation, as before, being that at higher temperatures a larger fraction of the electrons are in the quasi-free state. High pressure does just the opposite; it shifts the equilibrium in Equation 1 to the right. That is, the electron is localized a larger fraction of the time at high pressure causing a lower mobility.

In terms of Le Chatelier's principle this effect means that there is a decrease in volume for Reaction 1. From thermodynamics we have:

$$\Delta V_r = -RT\, d \ln K/dP. \tag{4}$$

Since the mobility is given by the mobility in the quasi-free state times the fraction of electrons in this state, then for the equilibrium given by Reaction 1 we have:[16]

$$\Delta V_r = RT\, d \ln \mu/dP.$$

The volume changes for Reaction 1 were evaluated from the mobility vs pressure curves. The magnitudes of the volume changes at 1 atmosphere and 25 C are -22, -28, and -19 cm^3/mol for *n*-hexane, *n*-pentane and 3-methylpentane, respectively.[16]

Equation 1 represents the localization of charge at a site in the liquid. Thus it is as if a large ion were formed. Large because the electron wavefunction is diffuse and extends out several molecular diameters. For reactions involving ions, electrostriction dominates the volume change and in non-polar solvents volume changes due to this effect are especially large.[18] The observed volume changes for Reaction 1 were attributed to electrostriction of the solvent around the trapped electron. The results are consistent with the classical theory of Drude and Nernst[19] which showed that the volume change ΔV_{es} due to electrostriction is given by:

$$\Delta V_{es} = (-z^2e^2/2R\epsilon^2)\,\frac{\partial\epsilon}{\partial P}, \tag{6}$$

where ϵ is the dielectric constant of the liquid. The experimentally observed volume changes depend linearly on the parameter $(1/\epsilon^2)\ \partial\epsilon/\partial P$ as required by Equation 6.

Branched hydrocarbons exhibit a very different effect of pressure. Figure 3 shows that for 2,2,4,4-tetramethylpentane the mobility *increases* with increasing pressure for all temperatures up to 100 C. At high pressure the mobility decreases with increasing temperature. For 2,2-dimethylbutane the results are shown plotted vs density in Figure 4A. Here also the mobility increases with pressure/density at low temperature and decreases with pressure at high temperature. At high pressure in this case there is little change with temperature.

For these branched hydrocarbons the energy of the localized electron is not sufficiently stable relative to the energy of the electron in the conduction band (V_o) so that the electron remains in the quasi-free state. Thus it is appropriate to ask how this behavior matches that expected for quasi-free behavior. To make this calculation using the deformation potential model requires a knowledge of the density dependence of V_o, the conduction band energy. As yet only measurements at 1 atm are available. Here the Wigner-Seitz model[20] was used to estimate the density dependence of V_o and its derivative. Only the first term in the series in Equation 3 was used. The theoretical mobility predicted by Equation 2 is shown in Figure 4B. The theory accounts for the general trends quite well. Namely, the theoretical mobility increases with increasing density at 23 C and decreases with increasing density at 100 C. Also little change is predicted at 60 C as is observed experimentally. Only the absolute magnitude is off; the theory predicts the mobility to be about a factor of two larger than observed. The agreement is good enough to support the assertion that what is observed in this branched hydrocarbon is quasi-free electron transport.

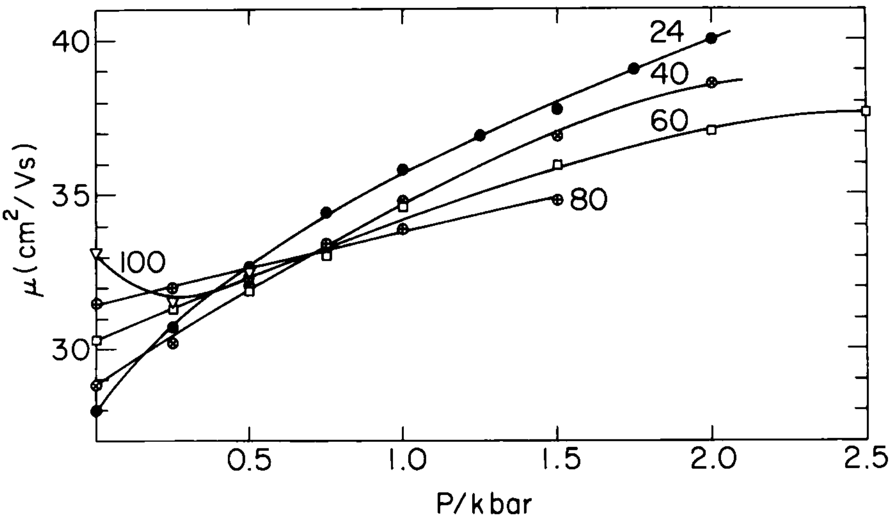

FIGURE 3 Electron mobility in 2,2,4,4-tetramethylpentane for pressures between 1 and 2500 bar, temperature in °C indicated on Figure.

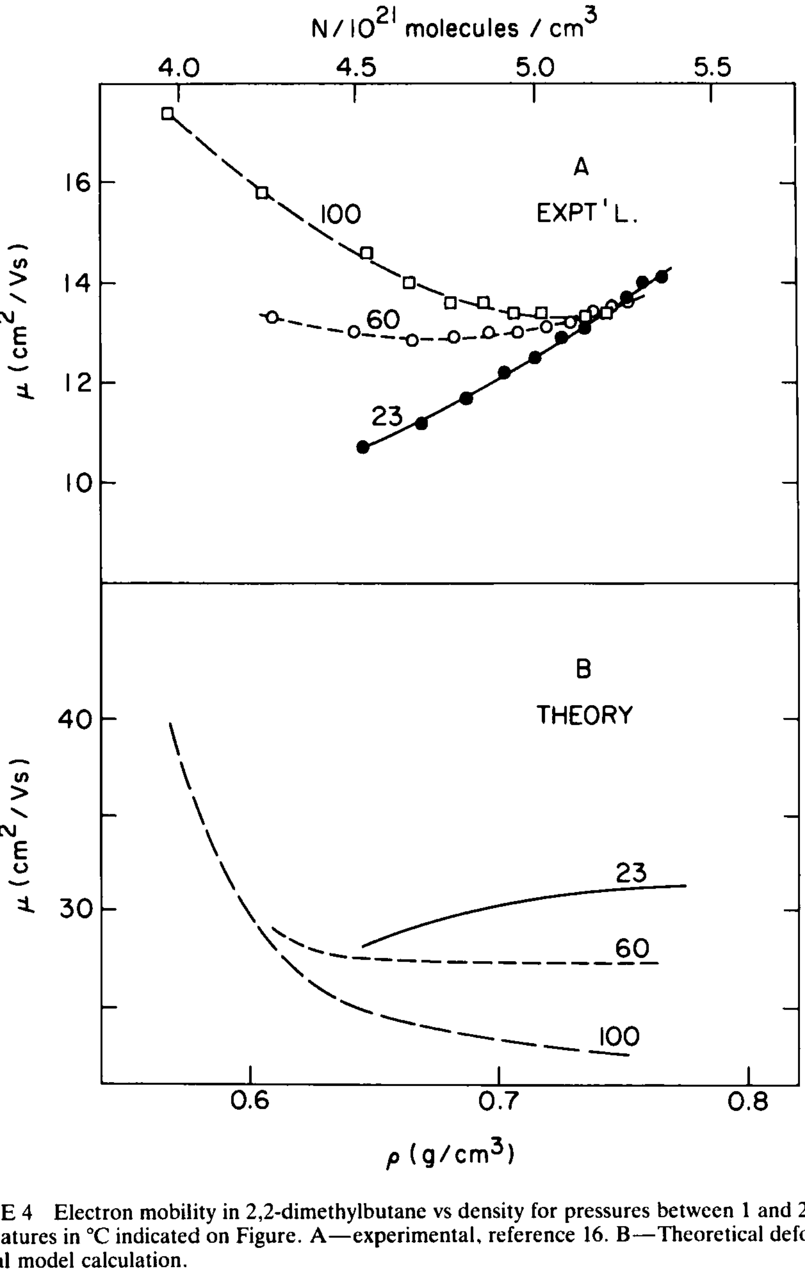

FIGURE 4 Electron mobility in 2,2-dimethylbutane vs density for pressures between 1 and 2500 bar. Temperatures in °C indicated on Figure. A—experimental, reference 16. B—Theoretical deformation potential model calculation.

An assumption of the deformation potential model is that Λ is larger than the wavelength of the electron.[12] For neopentane this assumption is satisfied but for 2,2-dimethylbutane Λ, as calculated from Equation 2, is only 8 Å at 20 C. The thermal wavelength is 17 Å for comparison. Although the restriction is not satisfied for 2,2-dimethylbutane the model gives a satisfactory representation of the results.

HALL MOBILITY

The mobility in the quasi-free state can be evaluated best by Hall mobility measurements. The Hall mobility is derived from an experiment in which the electrons are drifting in crossed electric and magnetic fields. Trapped electrons do not contribute to the signal; thus the Hall mobility (μ_H) in the case of organic liquids is essentially the mobility of the electron in the quasi-free state (μ_{qf}). So far, results are available only for five liquids; the data for room temperature are shown in Table II. Only liquids in which the drift mobility is fairly high have been studied. For four out of five of these branched compounds the drift and Hall mobilities are approximately the same. The exception is 2,2,4-trimethylpentane for which μ_D is about one-third of μ_H.

Another significant observation of these studies is that the Hall mobility varies with temperature. The biggest effect is observed for 2,2-dimethylbutane; μ_H increases by a factor of six over the range from 20 to 156 C. For this liquid as well as for tetramethylsilane and 2,2,4,4-tetramethylpentane the changes in drift mobility with temperature reflect changes in the Hall mobility. This is also true for neopentane up to 140 C.[21]

These Hall mobility measurements have been compared to those calculated by the deformation potential model. In this case terms involving derivatives of V_o greater than the first in the expansion in Equation 3 were neglected. The agreement between theory and experiment is quite good for 2,2-dimethylbutane[24] and for neopentane up to 140°.[21] Calculated and experimental mobilities differ at most by a factor of two. Thus the Hall mobility results confirm that for these branched hydrocarbons the electron is quasi-free.

Finally we note that for *n*-alkanes where the electron mobilities are low the conduction band energy (V_o) is high enough so that trapping is energetically favorable. In branched hydrocarbons where electron mobilities are high V_o is low and the electrons remain quasi-free. Why V_o is lower in branched than in *n*-alkanes is still not totally understood. The energy of this state is a function of the electron-molecule potential which at long range is attractive and at short range is repulsive. Recently, Plenkiewicz, *et al.*[25] used a modern, first-principles, pseudopotential and gas-phase scattering cross section data and successfully calculated V_o for the electron in liquid argon. Gas phase electron scattering cross sections are available for hydrocarbons, but are generally higher for the spherical than for the normal alkanes.[26] If suitable pseudopotentials can be developed and this theory extended to hydro-

TABLE II

Comparison of Hall and Drift Mobilities at 23°

Liquid	μ_H	Reference	μ_D	Reference
Neopentane	58, 85	21, 22	70.	2
Tetramethylsilane	101	23	100.	3
2,2-Dimethylbutane	11.6	24	10.5	16
2,2,4,4-Tetramethylpentane	32.	24	28	This Work
2,2,4-Trimethylpentane	22.	24	6.5	15

carbons then an explanation of this effect of molecular structure on electron transport properties may be found.

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