

Low energy electrons in non-polar liquids

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Abstract The properties of excess electrons in non-polar liquids have been studied for more than 30 years. Here, pertinent results are reviewed and discussed with respect to the possibility of studying electron–molecule interactions with low energy electrons in the liquid phase. Some new results on the estimate of the electron lifetime in the delocalized state in liquid hydrogen are presented.

Key words electrons • energetics • kinetics • non-polar liquids • lifetime

Introduction

A study of electron–atom and electron–molecule interactions in the gas phase has received a continuing interest since the early decades of the last century. This is related, e.g. to the important areas of plasma physics and plasma chemistry (gas discharges, plasma processing etc.) since in any kind of plasma electrons are by far the most abundant charge carriers [3]. More recently, the interaction of electrons with adsorbates on surfaces opened up new interesting areas of research. We mention here (i) substrate induced photochemistry where the interaction of photoexcited electrons from the solid substrate can control the photochemical behavior of an adsorbed molecule [5] or (ii) processes in STM (surface tunneling microscopy) where excitation, dissociation and desorption induced in single molecules by tunneling electrons is studied (single molecule engineering) [10].

The study of electron–atom or electron–molecule interactions in the liquid phase is complicated by the fact that electrons of defined energy interact strongly with the atoms or molecules comprising the liquid leading to a fast relaxation of the initial electron energy to the thermal energy of the liquid, $k_B T$. In non-polar liquids, it is possible by application of high enough electric fields to keep the electron collective at a certain mean energy which is determined by the field strength.

Table 1 lists the main physical and chemical properties of non-polar liquids. From a physical point of view – they are insulators. Due to the large ionization energy, I_{gas} , of the atoms or molecules comprising the liquid thermal excitation of charge carriers is absent. The self conductivity is usually caused by impurities, as for instance water, microscopic particles etc.

Upon condensation, a change of the ionization energy occurs which is given as,

$$(1) \quad I_{\text{liq}} = I_{\text{gas}} + P_+ + V_0 + E_{\text{val.}}$$

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Table 1. Physical properties of non-polar liquids.

Chemical composition	rare gases hydrocarbons and related compounds molecular gases (N ₂ , O ₂ , CF ₄ etc.)
Self conductivity	10 ⁻¹⁶ to 10 ⁻²⁰ Ω ⁻¹ cm ⁻¹
Ionization potential	6 to 24 eV
Electric dipole moment	μ = 0
Density	0.1 to 3 g/cm ³
Chemical properties	some chemically inert some toxic some flammable
Purity	rare gases >99.999 vol.% hydrocarbons >99.9 vol.% others >99 vol.%

Here, I_{liq} denotes the ionization energy in the liquid, i.e. the energy necessary to produce a positive ion and a delocalized electron in the conduction band. P_+ is the polarization energy of the positive ion, it is always negative, and V_0 gives the energy of the delocalized electron level in the liquid (bottom of conduction band), it can be smaller or greater than $E_{vac} = 0$. E_{val} is of the order of -0.1 eV and it denotes the change in the valence levels of the atoms or molecules upon condensation. The polarization energy can be estimated by a formula derived by Born [4],

$$(2) \quad P_+ = -\frac{e_0^2}{8\pi\epsilon_0 R} \left(1 - \frac{1}{\epsilon_r}\right),$$

ϵ_0 and ϵ_r are the dielectric constants of the vacuum and the liquid, respectively; e_0 is the charge of the electron; R is an ionic radius which can be estimated from the crystallographic radius or as a Wigner–Seitz radius given as,

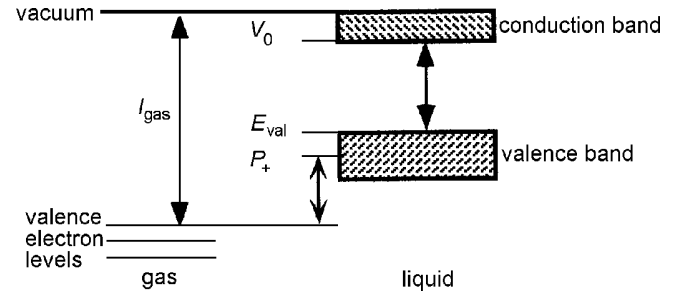
$$(3) \quad \frac{4\pi}{3} R^3 = \frac{1}{n},$$

where n denotes the number density of the liquid. Since P_+ is always negative it contributes to a reduction of the ionization energy in the liquid phase. V_0 can be either positive or negative. The energy levels in the gas phase and in the liquid phase are depicted schematically in Fig. 1. Typical values of the various quantities for different liquids are summarized in Table 2.

Table 2. Ionization energies, V_0 values, and P_+ values for various non-polar liquids with data from [15] and [20].

Liquid	T (K)	I_{gas} (eV)	I_{liq} (eV)	V_0 (eV)	P_+ (eV)	R_{ws} (Å)
helium	4.2	24.46	25.5*	+1.05	≈0	
neon	25	21.47	21.58*	+0.67	-0.59	1.87
argon	84	15.68	14.4*	-0.20	-1.08	2.25
krypton	116	13.93	11.56	-0.40	-1.97	
xenon	161	12.08	9.2	-0.67	-2.21	
methane	100	12.8	11.2*	-0.25	-1.38	2.08
<i>n</i> -heptane	295	10.2	8.6	+0.04	-1.56	
tetramethylsilane	296	9.79	8.1	-0.57	-1.12	2.95*
poly-methylphenylsiloxane	296	8.63	6.73	-0.90	-0.92*	

R_{ws} – Wigner–Seitz radius; * values estimated by means of Eqs (1), (2) and (3).

**Fig. 1.** Energy levels in the gas and liquid phases.

The present article is organized as following: we shall first summarize the various methods of electron injection and detection in non-polar liquids; in the following the drift velocity of electrons in pure liquids and in solutions as a function of the applied electric field strength is discussed; finally, a short description of electron–atom interaction in liquid neon, helium and hydrogen is given.

Methods of electron injection and detection

Since non-polar liquids are insulators, excess charge carriers have to be introduced by external means. In Table 3 the most important methods are summarized. The most prominent methods of electron injection are ionization by high energy radiation and by light.

Ionization by high energy radiation

High energy radiation (particles or quanta) interact with matter by ionization and excitation. The result of the initial ionization process are energetic secondary electrons which, in turn, produce tertiary electrons and so on till the energy of the electrons has fallen below the energy necessary to produce one electron–ion pair. The energy spent for the generation of one electron–ion pair (eV/electron–ion pair) is greater than the ionization energy in the liquid since part of the electron energy is spent in excitations. In the gas phase this energy is called the W-value. Its value is roughly two to three times the ionization potential. Since the high energy particles or quanta deposit their energy along tracks, the initial distribution of electrons and ions is inhomogeneous. A schematic representation of the ionization and excitation events produced by the passage of a high energy particle or a quantum is depicted in Fig. 2.

Table 3. Methods of electron injection.

Injection of electrons in non-polar liquids	
Ionization by high energy radiation	X-rays fast electrons UV-light elementary particles laser-induced multi-photon absorption
Photoelectric emission from metal or semiconductor cathodes	
Field emission from tips or blades	
Injection from the gas phase	low pressure discharge glow cathode
Semiconductor diodes	
Streaming liquids	

Electron-ion pairs which are separated by a few nanometers, only, recombine immediately after their production due to the strong Coulomb attraction (geminate recombination). Electron-ion pairs with a larger separation distance diffuse into the bulk of the liquid and, in the absence of an externally applied electric field, undergo volume recombination. Once the electrons diffuse into the bulk they are in thermal equilibrium with the atoms or molecules of the liquid. Electrons with mean energies greater than $k_B T$ exist in the liquid immediately after the ionization process. The electron leaves the positive ion with a kinetic energy of the order of 10 eV. In inelastic collisions with the atoms or molecules of the liquid they lose this excess energy and become thermalized. The thermalization time in molecular liquids is very short, smaller than picoseconds (see Figs. 3a and 3b), while in the heavier liquefied rare gases thermalization times from 1 ns in liquid Ar to 6 ns in liquid Xe have been measured [19]. The longer thermalization times in the rare gas liquids are due to the fact that at energies below the first electronically excited state only small energy losses due to elastic collisions are possible.

The superthermal electrons (electrons with a kinetic energy above kT) can interact with solutes. The analysis of such experiments and the extraction of kinetic data would be rather complicated.

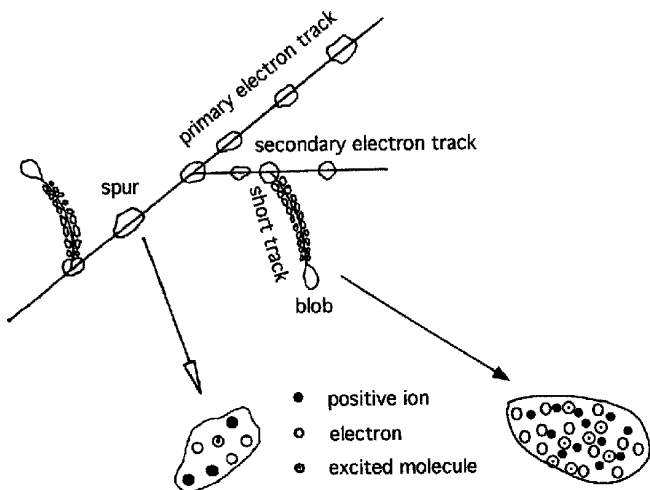


Fig. 2. Spatial distribution of ionization and excitations event produced by the passage of a high energy particle or a quantum.

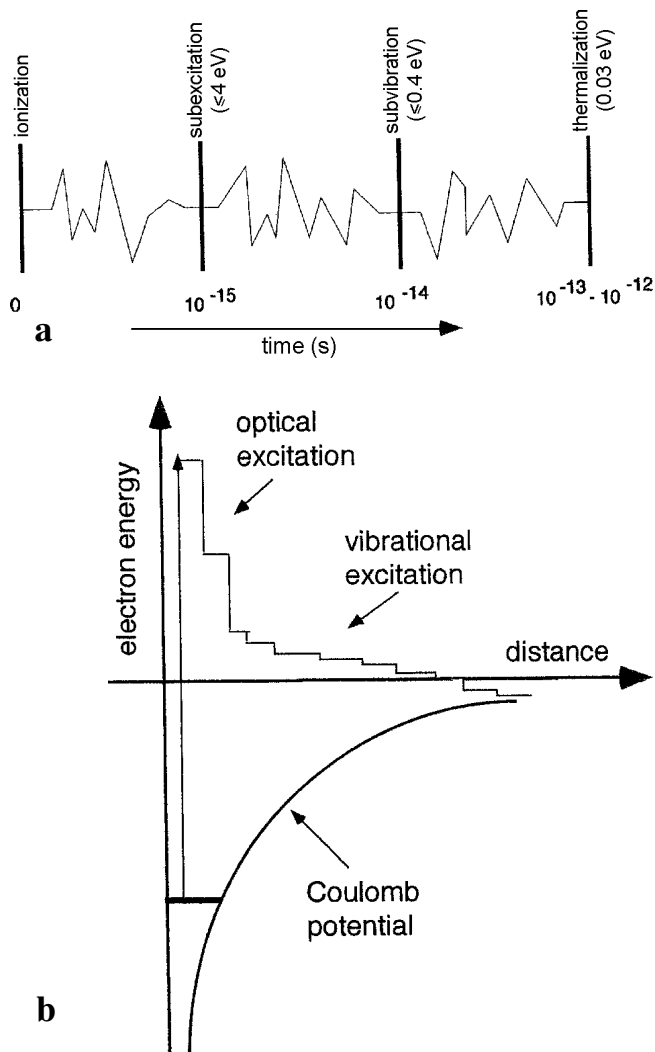


Fig. 3. a – The temporal evolution of the thermalization process; the zig-zag line is an artistic representation of the scattering events; b – the spatial evolution of the thermalization process in the Coulomb field of the positive ion.

Photoelectric injection from a metal cathode or photoionization

Electrons can be liberated from a metal cathode by photons of an energy exceeding the work function of the metal, W_{vac} . In contact with the liquid, the apparent work function, W_{liq} is given by,

$$(4) \quad W_{liq} = W_{vac} + V_0,$$

where V_0 is the energy of the bottom of the conduction band measured from the vacuum level, $E_{vac} = 0$. In the case of photoionization of atoms or molecules comprising the liquid or of solute molecules, Eq. (1) gives the photon energy necessary for the production of one electron-ion pair.

With the usual light sources, as high pressure xenon lamps or UV laser, the maximum kinetic energy of the liberated electron is of the order of 1 or 2 eV. These electrons lose their excess energy rapidly by elastic and inelastic collision and their final delocalized state is on the

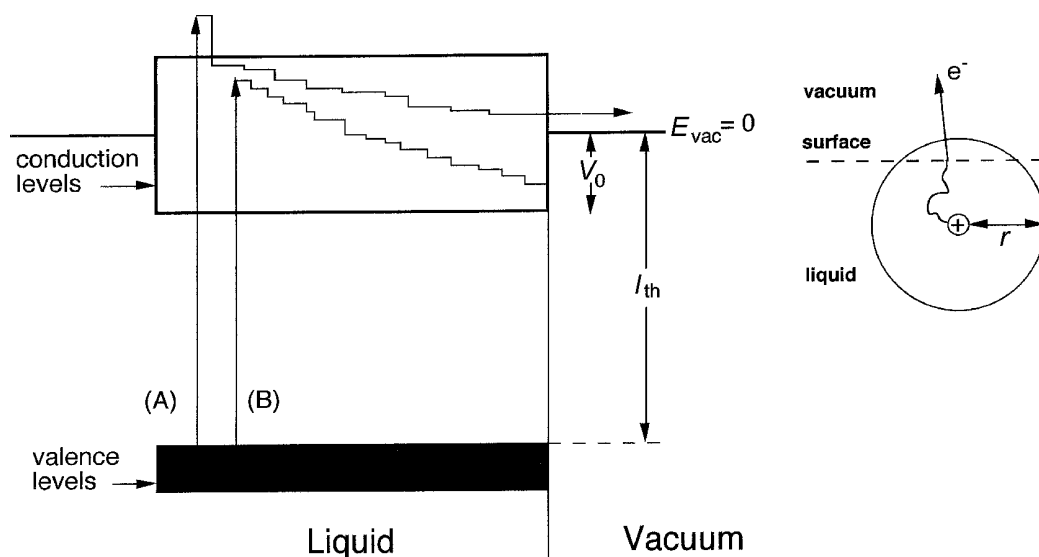


Fig. 4. Schematic representation of the VUV induced photoejection of electrons from a liquid into the vacuum; transition (A) depicts the energy of the ejected electron greater than the top of the conduction bend in the liquid; transition (B) depicts an electron which is injected into the conduction band of the liquid. Depending on their final energy they may (A) or may not (B) escape into the vacuum. I_{th} is the threshold energy for electron emission into vacuum (Eq. (5)).

bottom of the conduction band with thermal energy. In order to study the reactions of the superthermal electrons the reactant has to be close to the electron undergoing thermalization, which is experimentally difficult to achieve.

Other methods

All other methods of electron injection, which have been employed, yield electrons of a few eV kinetic energy which they lose rapidly in collisions and become thermalized. Field emission of electrons and injection from a semiconductor diode have the advantage of incorporation of the electron source into the measurement cell. Pulsed voltages allow the injection of electron pulses. Addition of grids allows the modulation of the electron current. The various methods are discussed in detail in the book by Schmidt [15].

Production of superthermal electrons by IR absorption of localized electrons

In certain non-polar liquids, the final state of the electron is a localized state. The electron is captured in a trap of several 0.1 eV depth. It exhibits an IR absorption. It is possible to briefly liberate the electron from this trap with photons of suitable energy [2]. Since the liberated electrons quickly lose their excess energy by collisions, they travel a few nm only before becoming trapped again. In principle, the study of reactions of these superthermal electrons with solutes should be possible.

Photoinduced electron emission into vacuum

Organic liquids with a low vapor pressure at room temperature are suitable for the study of VUV-induced electron emission from a liquid surface [8, 9]. The energetics of this process is given by the following equation,

$$(5) \quad I_{th} = I_{gas} + P_+ + E_{val}.$$

Here, I_{th} denotes the threshold energy for electron emission into vacuum. The penetration of the VUV light into the liquid is determined by the absorption coefficient of the liquid. An order of magnitude of 10^5 to 10^6 cm^{-1} is a reasonable estimate. It follows that the penetration length of the light is between 100 and 10 nm. Only electrons coming from the first few surface layers of molecules are able to escape before becoming thermalized. The process is schematically depicted in Fig. 4. Thin liquid layers on a substrate allow the interaction of photons or electrons with the molecules of the liquid layer.

Detection of electrons

The most sensitive detection methods make use of the high mobilities of excess electrons in these liquids which are 10 to 10^5 times greater than the mobility of the positive ions. Depending on the type of ionizing radiation and on the geometry of excitation, different current signals are obtained in a parallel plate dc-conductivity cell. Several examples are summarized in Fig. 5. Due to the great difference in mobility between electrons and positive ions it is easy to separate in time the current signals produced by the drift of these species. In Fig. 6, an example is shown of electron and ion drift in liquid methane.

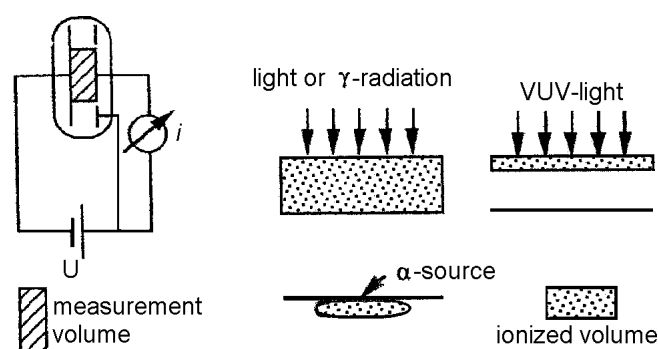


Fig. 5. Different methods of creating well defined regions of ionization in a parallel plate conductivity cell.

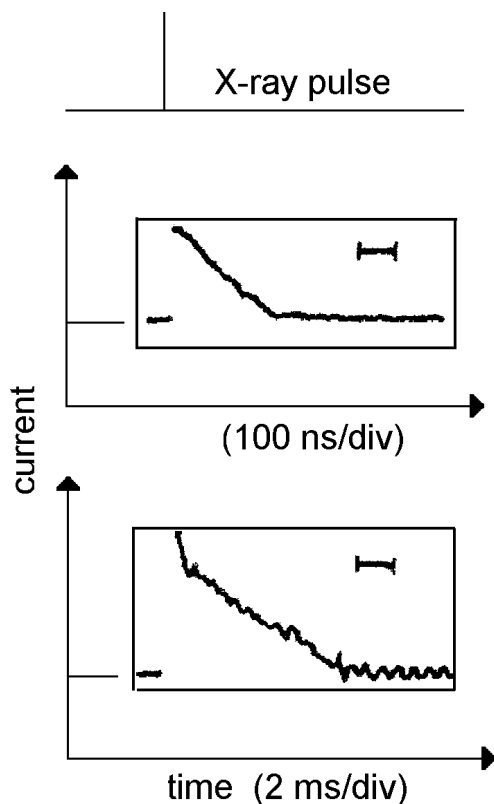


Fig. 6. Oscilloscopic traces of electron and ion currents in liquid methane at 111 K; ns trace – electrons; ms trace – positive ions.

Electron transport properties

The following transport properties of excess electrons in non-polar liquids have been studied: drift mobility, Hall mobility, electron–ion recombination, electron attachment.

An important transport property is the drift mobility, μ , which is given as the ratio of drift velocity, v_d at a given field strength, E ,

$$(6) \quad \mu = \frac{v_d}{E}.$$

At low field strength proportionality between v_d and E is measured and μ is constant. The electron collective is in thermal equilibrium with the liquid. In certain liquids, at higher field strengths, sub and super proportional dependencies of v_d on E have been observed. The mobility becomes a function of the applied field strength. The highest mobilities in non-polar liquids have been measured for the heavier liquefied rare gases, liquid Ar, Kr, and Xe. But, also in liquid methane, tetramethylsilane and neopentane, mobilities well over $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ have been observed. Representative data are summarized in Table 4. The important

Table 4. Electron mobilities in some non-polar liquids [15].

Liquid	T (K)	μ ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)
xenon	161	2000
krypton	120	1200
argon	84	500
tetramethylsilane	296	100
neopentane	296	65

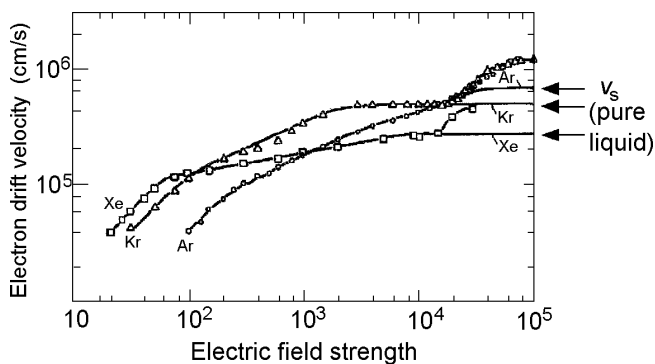


Fig. 7. Electron drift velocity as a function of the electric field strength for liquid Ar (87 K), liquid Kr (120 K) and liquid Xe (165 K) with a small concentration of nitrogen, which influences the dependence at high field strengths. The arrows indicate the drift velocity for the pure liquids, adapted from [21].

observation in these liquids is the dependence of the drift velocity on the applied electric field strength. Two examples are shown in Figs. 7 and 8. At higher fields, the electron collective produced by ionization or photoelectric effect reaches an equilibrium energy greater than $k_B T$. They pick up energy from the field and lose it by collisions and the net gain leads to a higher mean electron energy, ϵ . Various calculations have been performed for the liquefied rare gases [1, 7] and an example of ϵ as a function of E is shown in Fig. 9. A few data exist on the variation of the transversal diffusion coefficient in liquid Ar which relate to the electron mean energy. The data are included in Fig. 9. The agreement with the calculated curve is satisfactory. More experimental studies are necessary in order to establish a reliable dependence of the electron mean energy of the applied electric field strength. No calculations exist for molecular liquids.

With this field effect it is possible to study electron reactions with solute molecules in liquefied rare gases as a function of mean electron energy. In Fig. 10, the energy dependence of the electron attachment to N_2O in liquid Xe is depicted [1]. A maximum at 0.2 eV is observed. This effect can be rationalized by the assumption that the geometries of the neutral and the ion are different and the conformation energy has to be supplied by the electron.

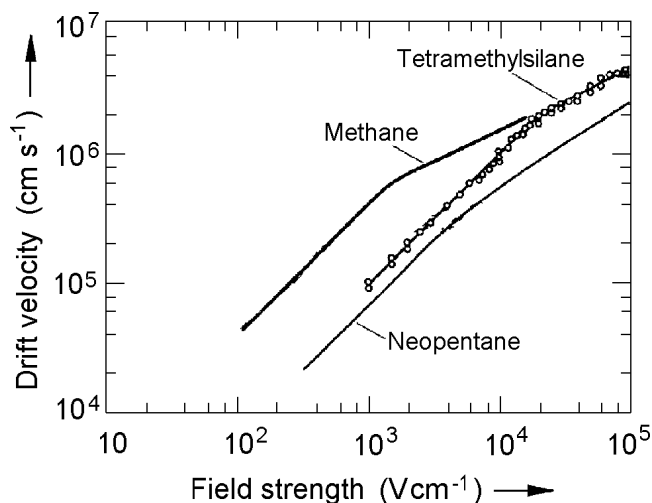


Fig. 8. Electron drift velocity as a function of the electric field strength for liquid methane (111 K), tetramethylsilane (295 K) and neopentane (295 K) adapted from [18].

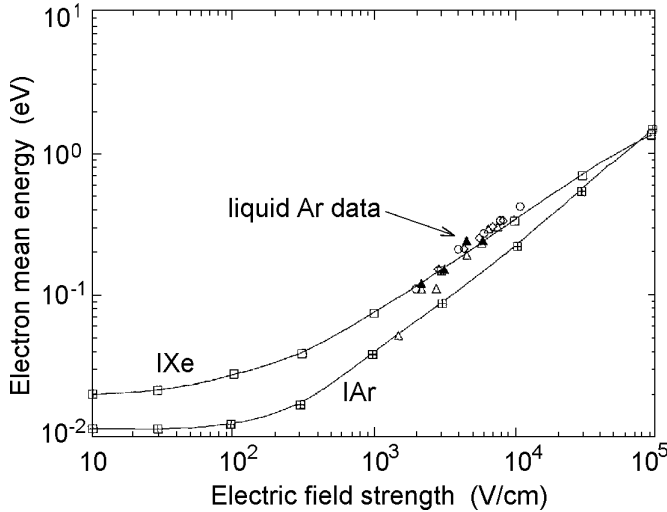


Fig. 9. Dependence of the electron mean energy as a function of the applied electric field strength in liquefied rare gases adapted from [1]; measured data points from [17].

Other examples exist, where added molecular solutes have an effect on the electron drift velocity at higher fields [1, 21].

Electron–atom interactions in liquid Ne, He, and H₂

Experiments have been carried out in which electrons were injected by photoelectric effect into liquefied neon [13], helium, and hydrogen [12]. When electrons are injected into a liquid they first move in the delocalized or extended state. Depending upon the electron-neutral interaction they become eventually localized or remain in the extended state. The electron-neutral interaction consists of exchange repulsion and polarization attraction. In liquid Ne, He, and H₂ the former interaction prevails, i.e., the average potential energy of an electron is positive, and the electron can only be captured by density fluctuations of the rare-faction type, microscopic voids or vacancies. In helium the electron trapping occurs very fast. The time for creation of the bubble was estimated to be of the order of picoseconds [11]. The process is depicted schematically in Fig. 11.

The transport process can then be described as follows. The electrons start at the cathode $x = 0$ with a drift velocity characteristic of delocalized electrons, v_{el} . During their

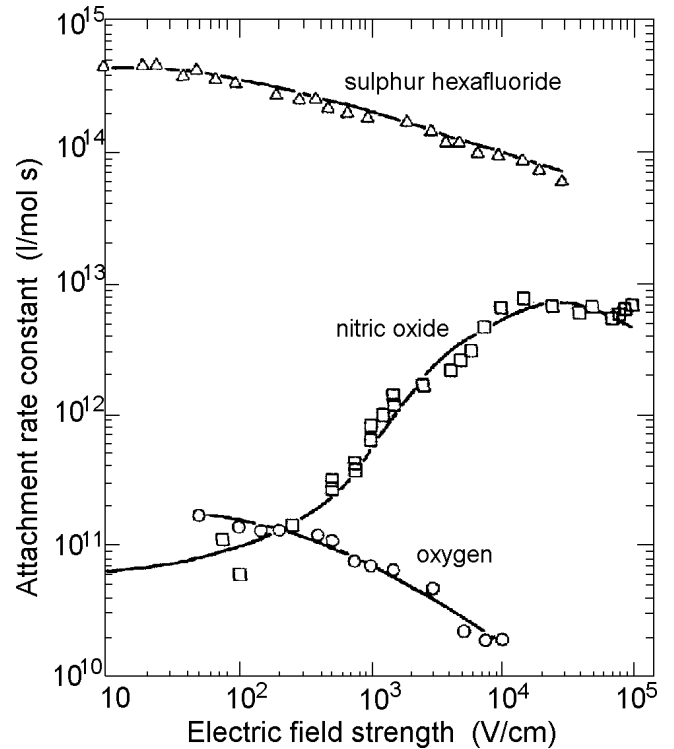


Fig. 10. Dependence of the electron attachment rate constant as a function of the applied electric field strength for several solutes in liquid Xe (165 K) adapted from [1].

lifetime, τ , as delocalized electrons they travel a distance, $d_{el} = v_{el}\tau$. This distance, d_{el} , can be considered as an attenuation length at which the number of delocalized electrons has been reduced to $1/e$. Transport as electron bubble takes place between d_{el} and d . The model is depicted schematically in Fig. 12. The apparent mobility is then obtained by d/t_d (t_d is the drift time obtained from the oscilloscopic trace with ms-time resolution), while the true drift velocity of the electron bubble, v_{loc} , is obtained as,

$$(7) \quad v_{loc} = \frac{d - v_{el}\tau}{t_d - \tau}$$

for liquid neon values of τ were measured to be in the range from 1 to 100 ns while the apparent drift times of the localized electrons were in the range of several 100 μ s, i.e. $\tau \ll t_d$. Then, equation (7) reduces to

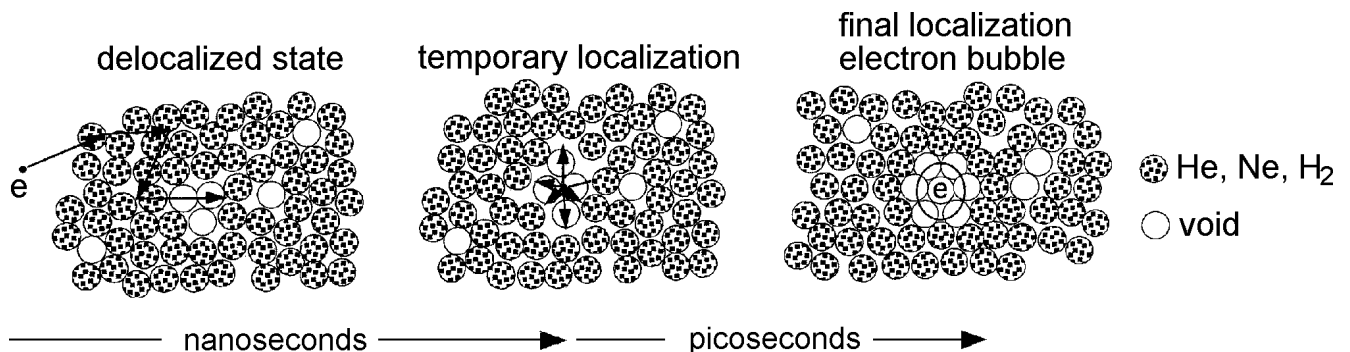


Fig. 11. Schematic representation of the localization process of electrons injected into liquid He, liquid Ne, and liquid H₂.

$$(8) \quad v_{\text{loc}} = \frac{d - v_{\text{el}}\tau}{t_d} = v_{\text{app}} - v_{\text{el}} \frac{\tau}{t_d},$$

where v_{app} denotes the apparent drift velocity of the electron bubble, that is the drift velocity obtained from the electrode separation d and the apparent drift time t_d obtained from the oscilloscopic trace. For τ , we obtain,

$$(9) \quad \tau = d \frac{v_{\text{app}} - v_{\text{loc}}}{v_{\text{app}}v_{\text{el}}}.$$

Measured data for liquid He and liquid H₂ are shown Fig. 13. We assume that the drift mobility of the electron bubble does not depend on the electric field strength (solid lines). The other information we need in order to evaluate τ by Eq. (9) is the drift velocity, v_{el} , in the delocalized state as a function of electric field strength. For the other rare gas liquids it was found that at field strength above 50 kV/cm the drift velocity, v_{el} , approaches saturation [21]. At such electric field strength the electron mean energy is far above the thermal energy of the liquid, $k_B T$. As a rough estimate one may take 1 eV as the order of magnitude at 100 kV/cm [1]. Since no values of v_{el} for liquid He are available, we plotted the data for liquid Xe, liquid Kr, liquid Ar [21], and liquid Ne [13] at the boiling point as a function of A^{-1} (A atomic mass) and obtained a data fit with a power plot of the slope of 3/4. Extrapolation yields a value of v_{el} for liquid He of 4×10^6 cm/s. With these data we estimate from Eq. (9) a lifetime of the delocalized electrons in liquid helium near the boiling point of $\tau \approx 5$ ns at 72 kV/cm applied electric field strength [16].

The validity of the present approach was tested with the data on liquid neon at 25 K [13], where the lifetime in the delocalized state and the mobility of the localized electron had been measured separately. From the field dependence of the drift velocity of the electron bubble, a lifetime at 55 kV/cm was estimated which agreed within a factor of two with the measured lifetime. The discrepancy is probably mainly due to the fact that saturation of the drift velocity of the delocalized electrons at 55 kV/cm has not been achieved, yet.

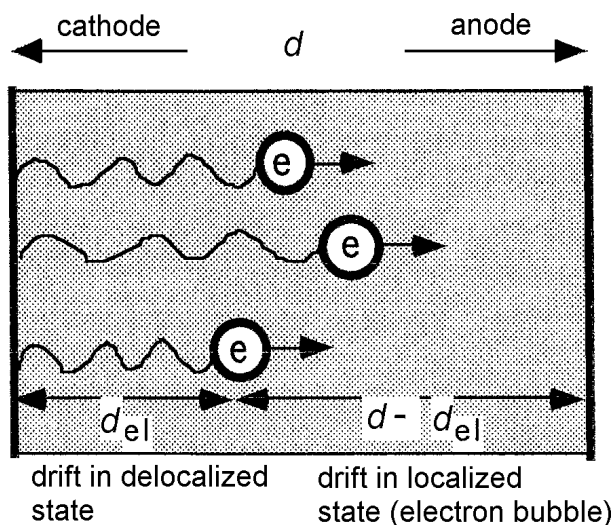


Fig. 12. Drift of electrons injected into liquid He, liquid Ne, or liquid H₂ in the delocalized and localized states.

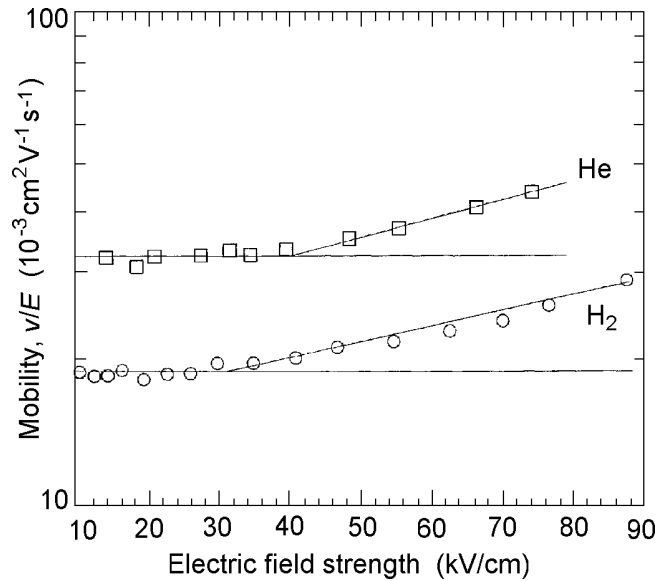


Fig. 13. Apparent drift mobility of electrons in liquid He (3.87 K) and liquid H₂ (20 K) as a function of the applied electric field strength adapted from [12].

The evaluation of the data for liquid hydrogen requires the saturation drift velocity v_{el} . No measurements are known for liquid H₂. The saturation velocity of electrons in two molecular liquid has been estimated. Measurements in liquid tetramethylsilane at 296 K gave a value of 7.8×10^6 cm/s [6] and measurements in liquid methane yielded 6×10^6 cm/s at 111 K [14]. These values give us the right order of magnitude. If we use 5.5×10^6 cm/s as the high field electron drift velocity in liquid H₂ we estimate a lifetime in the delocalized state of $\tau \approx (4.5 \pm 2)$ ns at a field strength of 88 kV/cm. In principle, this lifetime could be measured by conductivity methods.

Conclusions

The study of electron–atom or electron–molecule interactions of low energy electrons in non-polar liquids is at present restricted to liquids exhibiting a high electron mobility. Here, by application of a suitable electric field strength it is possible to maintain the electron mean energy at a given value, between $k_B T$ and a few eV. Cross section data can be extracted by taking into account the energy distribution function of the superthermal electrons.

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