Effect of CH$_4$ addition on excess electron mobility in liquid Kr

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Abstract

The excess electrons mobility $\mu$ has been measured recently in liquid mixtures of Kr and CH$_4$ as a function of the electric field up to $E \approx 10^4$ V/cm and of the CH$_4$ concentration $x$ up to $x \approx 10\%$, at temperatures $T \approx 130$ K, fairly close to the normal boiling point of Kr ($T_b \approx 120$ K).

We present here new data which extend the previous set in the region of low electric field. The experimental results are interpreted in terms of a kinetic model previously proposed to explain the concentration dependent behavior of $\mu$ in liquid Ar–Kr and Ar–Xe mixtures. The main result is that CH$_4$ is more effective in enhancing energy–transfer rather than momentum–transfer in comparison with mixtures of liquified noble gases. The field dependence of $\mu$ is quite complicate. In particular, at intermediate values of the field, there appears to be a crossover between two different electric–field dependent behaviors of $\mu$. The electric field strength at crossover is well correlated with the concentration of CH$_4$. This fact suggests that different excitations of the molecular solute might be involved in the momentum– and energy–transfer processes for different values of the mean electron energy.

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I. INTRODUCTION

The study of electron conduction in nonpolar liquids is of great fundamental and technical interest. Nonpolar liquids are examples of simple disordered materials. Theoretical investigations of the electronic states in such media are connected to experiment by the low field behavior of the excess electron mobility. The properties of excess electrons in such media may also give useful information on the electronic states in noncrystalline solids.

Nonpolar liquids are also used as sensitive media in high-energy physics ionization detectors. For such an application it is essential to know the behavior of excess electrons in the high-field region, where detectors are typically operated, in order to understand the basic electronic conduction mechanisms in that particular range for the goal of optimizing the detectors’ performances.

Liquified heavy noble gases, Ar, Kr, and Xe, are mainly used in ionization chambers because of the combination of large density and high values of the excess electron mobilities. At small electric fields mobilities exceeding several hundreds of cm$^2$/V s have been measured. In these so-called high-mobility liquids electrons are assumed to be quasifree because their mean free path is relatively long although they are moving in a very dense environment of atoms which are very effective scattering centers in the gas phase.

At small electric fields electrons are in near thermal equilibrium with the atoms of the host medium. The electron mobility is determined by processes of elastic scattering and is approximately independent of the field strength. In this region the drift velocity increases linearly with the field strength. At higher values of the field the electron drift velocity increases less than proportionally with the field and, finally, it nearly saturates. This behavior is related to the increase of the mean electron energy with the field and to the dependence of the scattering rate on the electron energy.

It has been shown that the addition of a molecular or atomic solute in small proportion influences the dependence of the mobility on the field strength, especially at high fields. In particular, the saturation drift velocity is largely increased above the value in the pure liquid. This effect is commonly explained as due to a reduction of the electron mean energy upon additional inelastic scattering with the impurities. These act as additional scattering centers that are very effective in thermalizing electrons even at quite large field strengths. In particular, for a spherical symmetric molecule like CH$_4$, the inelastic processes
are assumed to be due to the excitation of the main vibrational levels of the molecule (0.16 and 1.75 eV) upon collisions with energetic enough electrons.

The search for the optimum combination of base liquid and impurity for the best detector performance is far from being concluded.

These mobility measurements are obviously important for detectors’ designers. However, from a fundamental point of view these data may give additional hints for the description of the electron mobility in liquids, which is not yet completely understood. In fact, the theoretical treatment of the field behavior of the mobility in a pure liquid is far from being satisfactory.

The description of the electron mobility in the liquid can be approached from two completely opposite directions. The first approach is the so called single-scattering picture, essentially due to Lekner, in which electrons scatter off single atoms of the liquid or, more precisely, they undergo a binary collision with a single interaction potential that takes into account contributions from the potentials of nearby atoms. In this model, the two-term solution of the Boltzmann transport equation allows the calculation of an energy-dependent scattering cross section.

At the opposite extreme, the deformation potential theory of Basak and Cohen (BC) represents the motion of the quasi-free electrons in the liquid as that of a wave in a quasi-periodic structure. In this model the electron mobility in a liquid is determined by the scattering produced by fluctuations of the bottom of the conduction band due to the intrinsic density fluctuations of the liquid.

In the latter model, the addition of a solute is assumed to enhance the disorder inherent to a fluid by introducing concentration fluctuations in addition to the usual density fluctuations. In the former one, many-body and multiple scattering effects are included in the cross sections, which have now to be determined by a fit to the experimental data.

On one hand, the BC model has been adapted with reasonable success to mixtures of liquid hydrocarbons, where both solvent and solute are liquid at the same temperature. Unfortunately, its predictions have proven completely wrong when it is used for the description of the electron mobility in liquid mixtures of noble gases, namely Kr or Xe in liquid Ar.

A further drawback of the BC model, and of its extension to mixtures, is that it makes predictions only on the zero-field mobility and does not describe its electric-field dependence,
which, on the contrary, is very important from the point of view of detectors’ design.

On the other hand, the single-scattering (or gas-kinetic) approach has been successfully used to describe the electric field dependence of the electron mobility in liquid Ar and methane by introducing two constant scattering cross sections, the momentum- and energy-transfer cross sections, in the wake of Lekner’s theory. In this model, the many-body and multiple scattering effects due to the combined effect of short interatomic distances and large electron wavelength are embodied in the effective cross sections. This dressing of the scattering cross section due to multiple scattering effects is also at the base of the heuristic kinetic model, developed for the successful description of the electron mobility in dense noble gases.

The same gas-kinetic approach has proven also quite successful in the case of mixtures of liquified noble gases. Although in pure Ar and CH$_4$ the choice of two constant cross sections provides a quite nice agreement with the experimental data, an even better description of the electron mobility as a function of the electric field for all impurity concentrations in the mixtures of liquified noble gases is obtained by assuming a constant momentum transfer cross section $\sigma_m$ and an energy-transfer cross section $\sigma_E$ inversely proportional to the electron energy $\epsilon$, $\sigma_E \propto 1/\epsilon^2$. This dependence has been chosen only on a phenomenological basis and its meaning is not clear yet. However, since in this gas-kinetic model the cross sections are treated as adjustable parameters, it can be only said that this energy-dependent energy-transfer cross section provides a much better fit to the experimental data than a constant cross section does.

In this work we have therefore more carefully investigated the effect of the addition of the molecular solute CH$_4$ to pure liquid Kr, with emphasis on the low- and intermediate-field behavior of the mobility. Preliminary measurements, especially concerned with the mobility behavior at high fields, have been reported previously, keeping in mind the application of such mixtures in ionization detectors. We report here a more complete study that includes new measurements at quite small electric field strengths aimed at a more physical goal.

This goal is twofold. On one hand, this mixture has never been studied before and might be promising as a medium for ionization detectors. On the other hand, it represents a different benchmark for the validation of the gas-kinetic model and the determination of the concentration dependence of the effective cross sections might contribute useful pieces of information on the effectiveness of elastic and inelastic electron scattering processes in the
II. EXPERIMENT

The experimental apparatus has been described elsewhere and we refer to literature for the details. We recall here only the essential features of the experiment. The cell is a typical double–gridded ionization chamber. Excess electrons are photoextracted from a Ni–coated brass cathode by a short pulse of ultraviolet light produced by a Xe flashlamp. The four electrodes, anode, cathode and the two grids, are kept at suitable voltages in order to ensure the maximum grid transparency. Several guard rings are kept at the appropriate voltage by a resistor cascade in order to ensure the maximum field uniformity in the cylindrical drift space.

The electrodes are connected to charge amplifiers. The signal induced by the drifting electrons is recorded by a digital oscilloscope and analyzed by means of a personal computer. The drift time can be easily determined by analyzing the signal shape. To span a large region of electric fields in a single sweep both the drift times between the cathode and the first grid and between the first and the second grid are recorded simultaneously. The drift time in the region between the second grid and the anode, owing to the short distance and to the strong field between these two electrodes, cannot be measured reliably and has not been recorded. The two sets of drift mobility measured in the first and second region agree well with each other within the experimental accuracy where the field values overlap. The overall accuracy of the mobility measurements is better than 10%.

Very pure, commercially available gaseous mixtures of CH$_4$ in Xe of different and known composition are condensed in the cell through an Oxisorb purifier to remove oxygen and water vapor impurities. The cell is cooled down to the desired temperature by immersion in an isopentane bath cooled by liquid N$_2$. Two thermoresistors located in the cell near the cathode and the anode, respectively, provide constant monitoring of the temperature. The temperature is stable within ±0.5 K.
III. EXPERIMENTAL RESULTS AND DISCUSSION

The excess electron mobility in liquid Kr has been measured as a function of the electric field strength up to \( E \approx 10 \, kV/cm \) at \( T \approx 130 \, K \) for several mixtures of different composition. The liquid density of pure Kr at the temperature of the experiment is \( N \approx 167 \times 10^{26} \, m^{-3} \). The CH\(_4\) concentration, \( x \), of the mixtures is \( x = 0.01, 0.1, 0.5, 1, 2, 3, 5, \) and 10\%\), respectively. As a calibration we have also measured the mobility in pure liquid Krypton. Our data in the pure liquid agree well with literature data\(^4\).

We report the mobility as a function of the electric field strength \( E \) for several of the mixtures under investigation in Figure 1 and Figure 2 in order to avoid overcrowding of the figures. All mixtures show similar features.

As usual, the electron mobility \( \mu \) shows a low-field behavior where it is essentially independent of the electric field. In this region the excess electrons are in near thermal equilibrium with the atoms of the liquid, do not gain very much energy from the electric field, and mainly undergo elastic collisions that determine the mobility.

At higher fields, the mobility depends on the field strength and decreases sharply with increasing field. In this region the mean electron energy is greatly enhanced by the field and the net effect is a large increase of the scattering rate, leading to the observed decrease of the mobility. This behavior is common to all mixtures with some important differences.

At small concentration of methane the effect of the solute on the zero-field mobility \( \mu_0 \) is not very large. Only for the highest CH\(_4\) concentration (\( x \approx 10\% \)), there is a significant reduction of \( \mu_0 \), as shown in figure 3. Small concentrations, as evident from Figures 1 and 2, do mostly influence the high-field behavior of the mobility. An influence on momentum transfer is obtained only at high methane concentrations. This behavior is similar to that observed in mixtures of light alkanes in liquified noble gases\(^6\). However, this is the first time for this behavior to be observed in the present mixture of CH\(_4\) in liquid Kr.

Moreover, it has to be noted that the situation in mixtures of liquified noble gases is completely different as far as \( \mu_0(x) \) is concerned\(^2\). In fact, in the liquid Ar–Kr and liquid Ar–Xe mixtures, \( \mu_0 \) decreases rapidly with increasing solute concentration, especially in the Ar–Xe mixture. In the Ar–Kr mixture, where a concentration of \( \approx 30\% \) is reached, \( \mu_0 \) eventually levels off and becomes nearly concentration independent. In the Ar–Xe mixture, for concentration up \( x \approx 5\% \), \( \mu_0 \) decreases linearly with large negative slope as \( x \) is increased.
The sharp decrease of $\mu$ with increasing $E$ at larger fields (see Figures 1 and 2) is commonly attributed to the increase of the mean electron energy with increasing electric field. Between collisions, at higher fields, electrons pick up more energy from the field than they are able to share with the liquid upon collisions and thus become epithermal. The scattering rate is consequently enhanced and the mobility decreases.

The change of the electric field dependence of the mobility (see Figures 1 and 2) is therefore due to the increase of the mean electron energy above the thermal value because of the applied electric field. Upon increasing the methane concentration in the mixture, the region where the mobility is field independent spans a wider field range and the transition to the hot–electron behavior shifts to larger field strengths. Moreover, in the epithermal region, higher field strengths are required, upon increasing the impurity concentration, in order to achieve the same mobility value. Since $\mu$ depends on the mean electron energy only, provided that all other parameters are kept fixed, this fact means that electrons reach the same mean energy at larger fields for increasingly higher concentration of impurities.

These observations confirm the assumption that molecular impurities are very effective in thermalizing electrons at larger fields although they are not as effective as atomic impurities as far as momentum transfer is concerned. Molecular impurities act as additional scattering centers for electrons where they might lose energy in inelastic collisions more efficiently than in the pure liquid.

A similar behavior has been observed also in liquid mixtures of liquified noble gases, where atomic impurities Xe and Kr were dissolved in liquid Ar. Also in that case, atomic impurities extend the range of the thermal behavior of electrons. However, a stronger dependence of $\mu_0$ on the impurity concentration was observed. This behavior is probably related to the fact that atomic impurities have fewer inelastic scattering channels for low–energy electrons than molecular impurities do and affect more effectively the momentum–transfer– rather than the energy–transfer processes.

At high fields the drift mobility is determined essentially by the relative magnitudes of elastic and inelastic energy loss rate. When inelastic losses become greater than the elastic ones the drift mobility increases above the value of the pure liquid.

In order to carry out a simple analysis of the experimental data, we adopt the gas–kinetic approach of Kaneko et al., based on the two–term solution of the Boltzmann transport equation. For a simple fluid of number density $N$, the mobility $\mu$ is given by the usual
\[ \mu = - \left( \frac{e}{3} \right) \left( \frac{2}{m} \right)^{1/2} \int_0^\infty \frac{\epsilon}{N \sigma_m(\epsilon)} \left[ \frac{dg(\epsilon)}{d\epsilon} \right] d\epsilon \]  

(1)

where \( \sigma_m(\epsilon) \) is the energy–dependent momentum–transfer scattering cross section. \( e \) and \( m \) are the electron charge and mass, respectively. The Davydov–Pidduck electron energy distribution function \( g(\epsilon) \) is given by

\[ g(\epsilon) = A \exp \left\{ - \int_0^\epsilon \frac{dz}{k_B T + \left( \frac{M}{6m} \left( \frac{\epsilon E}{N} \right)^2 \right)^{1/2} \frac{1}{z \sigma_m(z) \sigma_E(z)}} \right\} \]

(2)

where \( M \) is the atomic (molecular) mass, \( \sigma_E(\epsilon) \) is the energy–dependent energy–transfer scattering cross section. The constant \( A \) is fixed by the normalization condition \( \int_0^\infty \sqrt{z} g(z) dz = 1 \).

From Eqns. (1) and (2) it is evident that the mobility is primarily determined by the momentum–transfer cross section, but the energy–transfer cross section also affects the mobility because it influences the electron energy distribution function by controlling the rate at which energy is exchanged.

Strictly speaking, in order to account properly for the scattering of electrons off correlated atoms in the fluid, Eq. (1) should be divided by the long–wavelength limit \( S(0) \) of the static structure factor, that takes into account the compressibility of the medium. However, according to Kaneko et al., we set \( S(0) = 1 \) and every correlation effect is now accounted for by the effective cross section determined in this way.

By introducing constant values for the two relevant cross section \( \sigma_m \) and \( \sigma_E \approx 100 \sigma_m \), this model reproduces quite well the low–field limit of the experimental mobility in liquid Ar and CH\(_4\), but is not very accurate in the high–field region.

A great improvement for the description of the mobility in this region has been obtained by introducing an energy–dependent energy–transfer cross section of the form

\[ \sigma_E(\epsilon) = \sigma_{E_0} \left( \frac{\pi k_B T}{\epsilon} \right) \]

(3)

where \( k_B \) is the Boltzmann constant and \( T \) is the temperature.

This particular choice is heuristic and does not rely on any theory. However, it is interesting to note that \( \pi k_B T / \epsilon \) is the square of the ratio of the de Broglie wavelength of an electron of energy \( \epsilon \), \( \lambda = h / \sqrt{2m \epsilon} \), to its thermal value, \( \lambda_T = h / \sqrt{2m \pi k_B T} \). In other words, it seems
that upon collisions the electron is exchanging energy with a cross section proportional to the cross sectional area of the associated quantum wavepacket. In order to test this view, mobility measurements should be carried out as a function of temperature. Anyway, we do not insist on this point since it is merely speculative.

With the introduction of the analytic form of $\sigma_E$ given in Eq. 3, the integrals in Eqns. 1 and 2 can be solved analytically, yielding

$$
\mu = \mu_0 \left[ 1 + \left( \frac{M}{6\pi m} \right) \left( \frac{eE}{N k_B T} \right)^2 (\sigma_m \sigma_{E_0})^{-1} \right]^{-1/2}
$$

with the usual expression for $\mu_0$

$$
\mu_0 = \frac{4e}{3N \sigma_m \sqrt{2\pi mk_B T}}
$$

It is easy to show that with this choice of $\sigma_E$, at high-fields $\mu \propto E^{-1}$, so that the drift velocity turns out to be approximately constant, as experimentally observed.

The extension of this model to binary mixtures is easily accomplished by introducing the concept of an equivalent one–component fluid with density $N$ and mass $M$ of the pure solvent (in this case, Kr) but described by effective scattering cross sections $\sigma_m(x)$ and $\sigma_{E_0}(x)$, which now depend on the solute concentration.

We have therefore analyzed the present data according to Ref. 20, by assuming, for each mixtures of concentration $x$, that the momentum transfer cross section is energy independent $\sigma_m(x,\epsilon) \equiv \sigma_m(x)$, and that the energy–transfer cross section is proportional to the inverse electron energy as described by Eq. 3 with $\sigma_{E_0} \equiv \sigma_{E_0}(x)$.

Eq. 4 has been fitted to the present experimental data with $\sigma_m$ and $\sigma_{E_0}$ as adjustable parameters. In figure 4 we show the values of the parameters resulting from the fit.

The momentum transfer cross section strictly reflects the behavior of $\mu_0$ as a function of the methane concentration. This is obvious by inspecting Eq. 3. Its value is $\sigma_m \approx (6 \div 7) \times 10^{-2} \text{ Å}^2$ and raises up to $\approx 9 \times 10^{-2} \text{ Å}^2$ at the largest methane concentration. These values can be compared to the value $(0.1 \div 0.4) \text{ Å}^2$ of the momentum transfer scattering cross section of atomic Kr at the Ramsauer minimum around $0.5 \div 0.7 \text{ eV}^{20}$.

In the present mixtures, $\sigma_m$ is approximately 3-4 times smaller than the value $\sigma_m \approx 0.2 \text{ Å}^2$ obtained for pure liquid Ar, as a result of the fact that also in pure liquid Kr electrons are more mobile than in pure liquid Ar. The behavior of $\sigma_{E_0}(x)$ is very different in comparison with that of $\sigma_m(x)$. It shows a large and almost linear increase with increasing methane concentration.
concentrations. At $x = 0$, $\sigma_{E_0} \approx 2 \, \text{Å}^2$, to be compared to the value $\sigma_{E_0} \approx 10 \, \text{Å}^2$ found in pure liquid Ar\cite{20}. For $x = 10\%$, $\sigma_{E_0} \approx 170 \, \text{Å}^2$. This confirms the fact that the increase of the concentration of methane in liquid Kr strongly enhances the inelastic processes leading to electron energy relaxation, while it has a nearly negligible effect on the processes of momentum transfer.

It is not completely surprising that the energy transfer cross section is much larger than the momentum transfer one because, as already pointed out in literature\cite{20,22,23}, the efficiency of energy transfer for thermal electrons is larger than that of momentum transfer by a factor $\approx 1/S(0) \gg 1$. In any case, we have to stress the fact that the behavior of the cross section with the concentration confirms the picture that the addition of a molecular solute increases the chance of an electron undergoing scattering.

In figure 5 we show the result of this kind of fit for the mixture with $x \approx 5\%$. A similar behavior is found in all mixtures. It is easily observed that Eq. 4 correctly fits the data only up to intermediate field strengths, of the order of several hundreds of $V/cm$, depending on the solute concentration. For larger values, $\mu$ decreases less rapidly with increasing $E$. Its field dependence changes from the $E^{-1}$ behavior, predicted by Eq. 4 with $\sigma_E$ given by Eq. 3, to a softer $E^{-1/2}$ behavior. This effect is observed for all mixtures.

This new kind of field dependence at large fields is typical for constant cross sections. Therefore, at larger fields, hence at larger mean electron energies, the scattering events determining the mobility resemble those due to a gas of hard spheres. However, we have to recall that this kind of language is more pictorial than real, because we are considering effective cross sections dressed by many body and multiple scattering effects in a gas–kinetic model rather than real two–body collisions.

In the same Figure 5 we show the prediction of the gas–kinetic model where we have introduced a constant $\sigma_E$, in order to simulate the results of hard–sphere scattering. The two curves in the figure have been obtained with $\sigma_E = \sigma_{E_0}$ (dashed line), with the value of $\sigma_{E_0}$ determined by the fit with Eq. 4, and with $\sigma_E = (2\pi/3)\sigma_{E_0}$ (dashed–dotted line), i.e., at thermal energy. In both cases, the calculated mobility at high fields is nearly parallel to the experimental data.

In any case, the deviation of the mobility from the $E^{-1}$–behavior towards the $E^{-1/2}$–one indicates that the processes of inelastic energy transfer are changing somewhat with the electron energy, as though different inelastic channels were opened by increasing the mean energy.
electron energy, leading to a different energy dependence of $\sigma_E$.

For the sake of completeness, it has to be noted that this change of behavior, though less relevant, is observed also in pure liquid Kr. A possible explanation of the effect in the pure liquid might be related to the possible existence of the Ramsauer minimum of the cross section also in the liquid, as argued by Christophorou et al. In this case, at high fields, the electron energy distribution function is very broad and the cross section would be averaged across the Ramsauer minimum, thus yielding approximately a constant value.

A careful inspection of the $\mu(E)$ data shows that $\mu$ deviates from the $E^{-1}$—behavior when it approximately has the same value (within a factor of order unity) for each mixture. In other words, the deviation takes place when the mean electron energy is approximately the same in all mixtures, independently of the methane concentration. This confirms the hypothesis that new inelastic channels related to the molecular impurity open up when the mean electron energy exceeds a given threshold.

To give an estimate of the effect, in figure 6 we plot the value $E^*$ of the field where $\mu$ takes on the value $\mu^*$ and starts deviating from the $E^{-1}$—behavior. This threshold electric field has a nice square–root dependence on the CH$_4$ concentration. This is easy to understand analytically if one inverts Eq. 4 with $\mu^*/\mu_0(x)$ and $\sigma_m(x)$ approximately constant, thus obtaining

$$E^* \approx \left\{ \frac{6\pi m}{M} \left[ \left( \frac{\mu_0}{\mu^*} \right)^2 - 1 \right] \left( \frac{Nk_B T}{e} \right)^2 \sigma_m \sigma_{E_0} \right\}^{1/2}$$

By inspecting figure 4 one observes that $\sigma_{E_0}(x)$ increases linearly, to a very good approximation, with $x$. Hence, $E^*$ is approximately proportional to $x^{1/2}$. This observation is another confirmation of the fact that electrons are more efficiently thermalized by increasing the impurity content of the mixture.

Within this gas–kinetic model, the mean electron energy can be calculated as $\langle \epsilon \rangle = \int_0^\infty z^{3/2}g(z)dz$, where $g(z)$ is given by Eq. 2. If the analytic form Eq. 3 for the energy–transfer cross section and a constant momentum–transfer cross sections are used, the mean electron energy turns out to be given by

$$\langle \epsilon \rangle = \frac{3}{2} \left[ k_B T + \left( \frac{M}{6\pi m k_B T \sigma_m \sigma_{E_0}} \right) \left( \frac{eE}{N} \right)^2 \right]^{1/2}$$

At the field $E^*$, where the high–field dependence of the mobility changes from $E^{-1}$ to $E^{-1/2}$, the mean electron energy takes on the value $\langle \epsilon \rangle^*$ shown in Figure 7. Beside a small decrease
with increasing concentration, $\langle \epsilon \rangle^*$ is close to 0.15 eV, quite consistent with the value 0.16 eV reported in literature\cite{4,21} for the excitation of the main vibrational level of CH$_4$. This result further confirms the conclusion that the change of the high-field behavior of the mobility is related to the opening of molecular inelastic channels of energy transfer.

IV. CONCLUSIONS

As observed in many other liquid mixtures, also in CH$_4$–doped liquid Kr the addition of molecular impurities increases the efficiency of electron thermalization. This fact permits to increase the drift velocity of electrons in the mixtures used as sensitive media in ionization detectors with respect to case of the pure liquid.

The use of the gas–kinetic approach also in liquid mixtures to describe the electric field dependence of the electron mobility gives very nice results. It is a very simple model that relies on a very easy physical picture to grasp, namely a binary–collisions picture. Nonetheless, in spite of its simplicity, the gas–kinetic model gives useful information about the relative strength of elastic and inelastic processes through the magnitude and concentration dependence of the effective cross sections, $\sigma_m$ for the momentum–transfer and $\sigma_E$ for the energy transfer.

In the case of CH$_4$–doped liquid Kr, the molecular solute has a relatively small influence on the momentum–transfer processes, as deduced from the fact that the zero–field mobility $\mu_0$ does not depend very much on the methane concentration. On the contrary, CH$_4$ impurities originate an efficient energy relaxation of excess electrons. This fact has the consequence that collisional ionization of the liquid mixture should be more difficult to reach, yielding higher breakdown fields in the mixtures than in the pure liquid.
Captions to the Figures

Figure 1 Electron mobility in pure liquid Kr (closed circles) and in several liquid Kr–CH$_4$ mixtures. Solid triangles: $x = 0.5\%$. Solid squares: $x = 5\%$. Open circles: $x = 10\%$. $x$ is the methane concentration. The error bars, of the order 5–10\%, are not shown for the sake of clarity.

Figure 2 Electron mobility in several liquid Kr–CH$_4$ mixtures. Closed diamonds: $x = 0.01\%$. Solid triangles: $x = 0.1\%$. Open squares: $x = 1\%$. Closed squares: $x = 2\%$. Open circles: $x = 3\%$. $x$ is the methane concentration. The error bars, of the order 5–10\%, are not shown for the sake of clarity.

Figure 3 Zero–field electron mobility as a function of the concentration $x$ of CH$_4$ in liquid Kr. The solid line is a parabolic fit to the data drawn to guide the eye.

Figure 4 CH$_4$ concentration–dependent behavior of the momentum–transfer cross section $\sigma_m$ (closed circle) and of proportionality constant $\sigma_{E_0}$ of the energy–transfer cross section $\sigma_E$. The solid lines are only guidelines for the eye.

Figure 5 Excess electron mobility as a function of the electric field in the mixture with $x = 5\%$ of methane. Solid line: fit of the kinetic model with the energy–transfer cross section inversely dependent on the electron energy. Dashed– and dot–dashed lines: prediction of the kinetic model with two different values of an energy–independent energy–transfer cross section.

Figure 6 Concentration–dependent behavior of the electric field values $E^\star$ beyond which the mobility data are no longer well described by an energy–transfer cross section inversely proportional to the electron energy. The solid line is a square–root fit to the data.

Figure 7 Dependence on the CH$_4$ concentration of the mean electron energy $\langle \epsilon \rangle^\star$ evaluated at the field $E^\star$ where the high–field behavior of the electron mobility changes from the $E^{-1}$ to the $E^{-1/2}$ dependence. The solid line is only a guide for the eye.
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$\mu$ (cm$^2$ /Vs)

$E$ (V/cm)
\[ \mu \text{ (cm}^2/\text{V s)} \]

\[ E \text{ (V/cm)} \]
$\mu_0$ (cm$^2$/V s) vs $x$ (%)
