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The influence of multiple scattering processes on the electron mobility in low density methanol gas

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The electron drift mobility μ has been measured in CH₃OH gas in the temperature range $303 \leq T \leq 363$ K and in the number density range $2.4 \times 10^{17} \leq n \leq 2.1 \times 10^{19}$ cm⁻³. It is usually assumed—although there is no foundation for it—that at such low gas densities the “zero-field” density-normalized mobility (μn) does not depend on n , i.e. it can be described by the so-called Lorentz single collision approximation [see, e.g., N. Gee and G. R. Freeman, *Can. J. Chem.* **61**, 1664 (1983)]. We observed, however, a density dependence of (μn) which can be explained approximately in terms of coherent and incoherent multiple scattering corrections where the coherent contribution due to correlations between the scatterers predominates at lower temperatures.

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I. INTRODUCTION

In order to study the transport of electrons in a moderately dense disordered fluid of polar scatterers as a function of the fluid number density n one usually starts with measurements of the electron mobility at—more or less—low gas densities. In this case it is generally assumed that the mobility of thermal electrons can be described within the margin of experimental error by the classical Lorentz limit (single scattering approximation)¹

$$\mu_L = -\frac{4\pi}{3} \frac{e}{m_e} \int_0^\infty (\partial f(\epsilon)/\partial \epsilon) (2m_e \epsilon)^{3/2} (\Gamma^m(\epsilon))^{-1} d\epsilon, \quad (1)$$

where $\epsilon = (\hbar k)^2/2m_e$ is the kinetic energy of the electron. The density of states $f(\epsilon) = (m_e/2\pi k_B T)^{3/2} \exp\{-\epsilon/k_B T\}$ has the form corresponding to that of a free electron gas. The quantity $2\Gamma^m(\epsilon)$ stands for the transport collision frequency. In the single collision approximation it depends on n , on the total momentum transfer cross section $\sigma_m^{av}(\epsilon)$, and on the relative velocity $(2\epsilon/m_e)^{1/2}$ of the electron with respect to the scatterer, i.e.,

$$2\Gamma_0^m(\epsilon) = n \sigma_m^{av}(\epsilon) (2\epsilon/m_e)^{1/2}. \quad (2)$$

For dipole molecules in the point-dipole limit $\sigma_m^{av}(\epsilon)$ takes the following form within the Born approximation²

$$\sigma_m^{av}(\epsilon) = (4\pi/3) (De/\hbar)^2 m_e / \epsilon, \quad (3)$$

where D is the dipole moment of the scatterers (the index av indicates the averaging over the dipole orientations).

In this classical single collision approximation the density normalized mobility ($\mu_L n$) should not depend on n at very low gas densities where the de Broglie wavelength of the electron, $\lambda_T = \hbar/(2m_e k_B T)^{1/2}$, is much smaller than its

elastic mean free path, $L = 1/(\sigma_m^{av}(\epsilon)n)$. The thermal average of the momentum transfer cross section in L is given by

$$\langle \sigma_m^{av}(\epsilon) \rangle = 4\pi \int_0^\infty \sigma_m^{av}(\epsilon) f(\epsilon) [2\epsilon/m_e^3]^{1/2} d\epsilon. \quad (4a)$$

Taking into account Eq. (3) one has for a pure point-dipole rotator

$$\langle \sigma_m^{av}(\epsilon) \rangle^{\text{theor}} = A m_e / k_B T \quad \text{with} \quad A = (8\pi/3) (De/\hbar)^2. \quad (4b)$$

The unknown quantity in this description—the thermally averaged momentum transfer cross section $\langle \sigma_m^{av}(\epsilon) \rangle$ —is obtained experimentally in the following way: The drift velocity of thermalized electrons in low density gas is determined as a function of the electric field strength. The electron mobility is obtained from the drift velocity in the limit of zero field (“zero-field” mobility). Assuming that the “zero-field” density-normalized mobility (μn) does not depend on n , $\langle \sigma_m^{av}(\epsilon) \rangle^{\text{exp}}$ is then calculated from Eqs. (1)–(4).

It was found that the Born result is sometimes inadequate for analyzing the experimental data in detail.³ Therefore, several attempts have been made in the past to replace the Born scattering cross section [Eq. (3)] by a generalized ansatz $\sigma_m^{av}(\epsilon) = A_\alpha / \epsilon^\alpha$ with $\alpha \neq 1$ to obtain more accurately the magnitude and the energy dependence of the scattering cross section. For example, Gee and Freeman⁴ have measured the electron mobility in low density methanol gas at $293 \leq T \leq 617$ K. The (μn) data for the experimentally adjusted gas densities 2.9×10^{18} cm⁻³, 4.0×10^{18} cm⁻³, 7.0×10^{18} cm⁻³, and 3.07×10^{19} cm⁻³ as a function of T were all put together (see Fig. 5 of Ref. 4) in order to determine from the temperature dependent mean values $\mu n(T)$ the energy dependence of the electron momentum transfer cross section of methanol. However, Gee and Freeman have never tested if such an averaging procedure is really justified in this relatively large density range $2.9 \times 10^{18} \leq n \leq 3.07 \times 10^{19}$ cm⁻³. From experiments on rare gases it follows already that there is always a density effect of the “zero-field” density-

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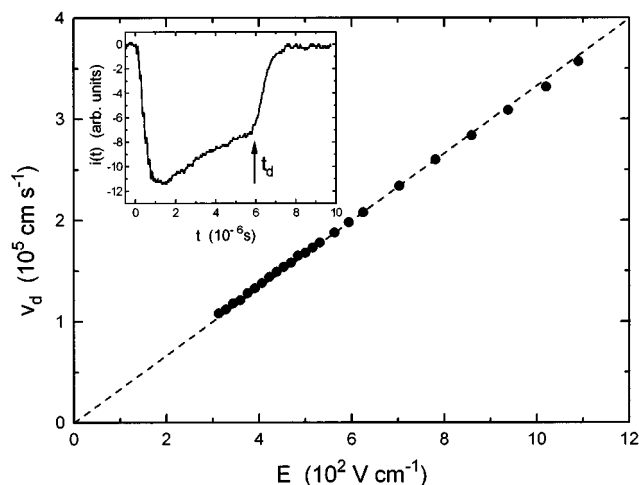


FIG. 1. Swarm drift velocity v_d as a function of the electric field strength E for electrons in low density CH_3OH gas ($T=333\text{ K}$, $n=1.22\times 10^{19}\text{ cm}^{-3}$). The inset shows the recorded electron current waveform for $E=313\text{ V cm}^{-1}$. A part of the electrons is captured during the drift by CH_3OH forming anions. The dashed line points out the linear relationship between v_d and E .

normalized mobility linear in n down to the smallest number densities, which is also fairly well understood theoretically.^{5,6} From our own electron mobility measurements in *high density* sub- and supercritical CH_3OH ($393\leq T\leq 573\text{ K}$, $2\times 10^{19}\leq n\leq 3.6\times 10^{21}\text{ cm}^{-3}$) we have got some hints that a density dependence of (μn) should be observable even for $n\leq 10^{19}\text{ cm}^{-3}$ — at least at lower temperatures.⁷ In this paper we present now the results of our investigation of the density and temperature dependence of the electron mobility in *low density* CH_3OH gas.

II. EXPERIMENT

The mobility of electrons was measured by the so-called pulsed Townsend method: Electrons were photoinjected from a stainless-steel photocathode into CH_3OH gas by a short laser pulse (Nd-YAG laser: $\lambda=266\text{ nm}$, pulse duration $<20\text{ ns}$, pulse energy $<8\text{ mJ}$). The swarm of about 10^4 to 10^5 electrons is drifting under the influence of an applied electric field E with the drift velocity v_d giving rise to a constant induced current $i(t)$ through a load resistor R_L which drops to zero when all the electrons are collected by the anode at a distance d from the photocathode. For each temperature, number density and field strength setting up to 100 signals were software averaged to improve the signal-to-noise ratio. The experimentally observed electron current pulse duration t_d in CH_3OH is in the order of 500 ns to $20\text{ }\mu\text{s}$ depending on E and the gas number density n . From the experimental linear relationship between $v_d=d/t_d$ and E , the mobility μ was determined from $\mu=v_d/E$ in the limit of zero field (see Fig. 1).

In connection with the electron mobility measurements in HCN (Refs. 8, 9) we have developed a drift cell made out of Duran glass with quartz windows, and an electrode assembly made out of stainless steel. The distance d between the photocathode and the anode can be varied between 0.10 and

$0.64\pm 0.01\text{ cm}$. This cell withstands pressures up to 40 bar for temperatures $T\leq 400\text{ K}$. Different thermostated pressure sensors can be coupled to the drift cell to measure the gas pressure in the drift space with an accuracy of $\pm 0.6\text{ mbar}$ for the gas pressure range $p\leq 200\text{ mbar}$ and with $\pm 2.5\text{ mbar}$ for $p\leq 1\text{ bar}$.

The drift cell is also provided with a reservoir for about 10 ml of CH_3OH purified by us in the following manner: Methanol (Merck, p.a. 99.8%) with a small amount of NaBH_4 (Aldrich) was refluxed for at least 3 h . Then it was fractionally distilled from the residues through a 20 cm Vigreux column. The middle fraction (about 50%) was collected and kept in a reservoir attached to a vacuum line (better than $1\times 10^{-6}\text{ mbar}$). The drift cell was then connected with the vacuum line in order to condense CH_3OH in the reservoir of the drift cell. Thereafter, CH_3OH was made free of electron scavengers such as O_2 and CO_2 by at least 10 “freeze-pump-thaw” cycles. It should be pointed out that all parts of the apparatus which came in contact with CH_3OH , in particular the drift cell, are cleaned with several organic solvents and were finally rinsed with overheated water vapor for at least 24 h .

The drift cell was then transferred into a steel tank filled with fine sand as a heat conducting medium. With an electrical heating system with PID-regulation units (Eurotherm) the chosen temperature in the cell could be held constant to within $\pm 0.5\text{ K}$. The temperature was controlled by NiCr-Ni thermocouples and by Pt 100 thermoresistors which were mounted on different positions at the drift cell.

The gas pressure in the drift cell could be adjusted by carefully opening of a valve of the filled drift-cell connected with the vacuum line or by controlled filling of the empty drift cell. The gas pressure and temperature readings were converted to values of the number density n of CH_3OH by using a virial equation of state from the literature.¹⁰ Further experimental details will be published in Ref. 9.

III. RESULTS AND DISCUSSION

In Fig. 2 we present the experimentally observed “zero-field” density-normalized mobility (μn) of electrons in CH_3OH as a function of n for the temperatures 303 , 333 , and 363 K . For some experimental points we have drawn the maximum error calculated by the method of error propagation. The large errors at low densities are due to the maximum possible errors of the used pressure sensors mentioned above. The (μn) -isotherm for $T=333\text{ K}$ has been measured several times and by different experimentators. Thus it demonstrates the reproducibility of these experiments. The results for the density range $2.4\times 10^{17}\leq n\leq 2.1\times 10^{19}\text{ cm}^{-3}$ show—in contrast to the measurements of Gee and Freeman—in fact remarkable deviations from the classical Lorentz transport [Eq. (1)] presented as horizontal curve (for $T=363\text{ K}$) in this plot. This means that in polar gases like CH_3OH the density dependence of (μn) *cannot* be neglected at such low gas densities. At constant temperature the observed decrease of (μn) with increasing gas number density n is linear in n as demonstrated by the dashed lines deter-

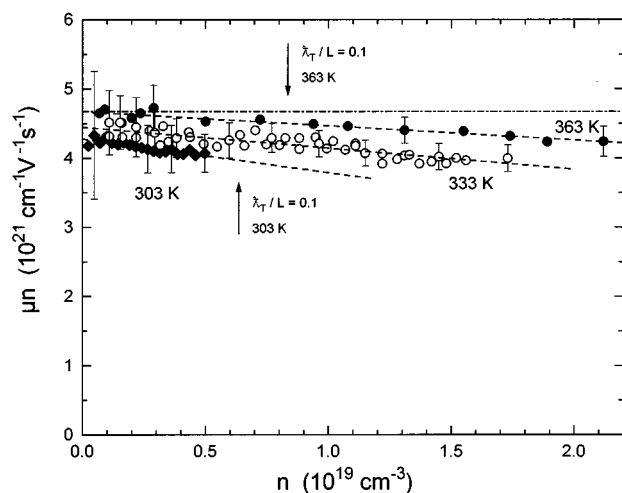


FIG. 2. Density normalized mobility (μn) of excess electrons in methanol gas as a function of n (for $2.4 \times 10^{17} \leq n \leq 2.1 \times 10^{19} \text{ cm}^{-3}$) at various temperatures: \blacklozenge , 303 K; \circ , 333 K; \bullet , 363 K; -----, classical Lorentz behavior, Eq. (1); ---, linear regression. The error bars represent the maximum calculated experimental uncertainties. The arrows sign those densities where the de Broglie wavelength λ_T of thermal electrons ($T=303$ and 363 K) is just one tenth of their mean free path L .

mined by linear regression. The negative slope becomes steeper with decreasing temperature. All this happens in a gas density regime where $\lambda_T/L \ll 1$.

We want to explain these experimental density and temperature dependencies as being produced by multiple scattering effects among which we consider the mean free path reduction due to quantum interference and due to correlations among the scatterers. Therefore, it is necessary to recall a few fundamental theoretical facts.

Because of the very long-range interaction between the electrons and the *polar* molecules of CH_3OH one has to take into account the influence of interference in multiple scattering on the collision frequency already at these very low gas densities. It was shown for the first time by Polischuk¹¹ theoretically within the framework of the Green's function method¹² that in such a case the momentum transfer collision frequency $2\Gamma_0^m(\epsilon)$ in Eq. (2) has to be replaced by the enhanced value $2\Gamma_1^m(\epsilon) = 2\Gamma_0^m(\epsilon)[1 + (0.5\pi - 0.6) \times \hbar \sigma_m^{av}(\epsilon)n/k]$. Its substitution in Eq. (1) followed by the expansion of the denominator in a power series in n yields approximately

$$\mu n \approx \mu_L n \left\{ 1 - \frac{\pi^{1/2}}{8} (0.5\pi - 0.6) \lambda_T \langle \sigma_m^{av}(\epsilon) \rangle n \dots \right\} \quad (5)$$

for $\lambda_T/L \leq 1$.

The theoretical calculation of this first order correction proportional to $\lambda_T \langle \sigma_m^{av}(\epsilon) \rangle n \equiv 1/k_T L$ (where k_T is the electron thermal wave vector) was performed by Polischuk under the following important assumptions:

- (i) The polar scatterers are considered as point-dipoles.
- (ii) The pure charge-dipole electron-scatterer interaction was considered in the Born approximation. Strictly speaking, the Born approximation is valid only when

$D \ll 2.5$ Debye (for comparison $D(\text{CH}_3\text{OH}) = 1.70$ Debye). This compromise allows to analyze in detail the multiple scattering effects.

- (iii) Correlations between the scatterers either in position or in orientation were, however, *ignored*.

Equation (5) differs slightly from that given by Polischuk [Eq. (16) in Ref. 11]. The original formula has been modified by us in order to take into account the mean Born scattering cross section defined by Eq. (4b). However, since the experimental scattering cross sections are sometimes almost twice as large as the Born ones^{13,14} it was already proposed by Polischuk to use in Eq. (5) the experimental scattering cross section. $\langle \sigma_m^{av}(\epsilon) \rangle^{\text{exp}}$ is obtained from

$$\langle \sigma_m^{av}(\epsilon) \rangle^{\text{exp}} = \frac{8e}{3} (2/\pi m_e k_B T)^{1/2} [(\mu n)_0]^{-1}, \quad (6)$$

where $(\mu n)_0$ is the experimental density-normalized mobility in the limit $n \rightarrow 0$. Eq. (6) implies, to maintain consistency, that the scattering cross section has a ϵ^{-1} energy dependence leading to Eq. (4b) but A is now a fit parameter. Finally we shall see that this restriction is correct.

It was shown by us that electrons in NH_3 gas ($D=1.47$ Debye) at moderate densities—at least for $n \leq \lambda_T / \langle \sigma_m^{av}(\epsilon) \rangle^{\text{exp}}$ —can be described almost quantitatively by Eqs. (5) and (6) in the temperature range $300 \leq T \leq 650$ K.¹⁵

We have already noticed that the first order correction due to incoherent multiple scattering [Eq. (5)] alone cannot completely describe the observed density dependence of (μn) in CH_3OH gas at higher densities for $T \geq 393$ K. Therefore, attempts were made to show that in polar gases correlations between the scatterers might be of some significance in the density range under consideration.⁷ It is well known that the static structure factor $S(\mathbf{q})$ which is related to the static correlation between the scattering sites in the medium described by the pair correlation function¹⁶ enhances the single collision momentum transfer cross section of rare gas atoms.¹⁷ For correlated dipole molecules the single collision momentum transfer or diffusion cross section measured by the Townsend method has to be replaced by

$$(\sigma_m^{av}(\epsilon))_{\text{correl}} = \int_0^{2\pi} \int_0^\pi (1 - \cos \theta) \times \left[\frac{4}{3} (D e m_e / \hbar^2)^2 \frac{1}{2k_0^2 (1 - \cos \theta)} \right] \times S(|\mathbf{q}|) \sin \theta d\theta d\phi, \quad (7)$$

where $|\mathbf{q}| = k_0[2(1 - \cos \theta)]^{1/2}$ is the momentum transfer, θ is the angle between the incident \mathbf{k}_0 and scattered \mathbf{k} electron wave vector. The term in the square brackets of Eq. (7) is just the total differential cross section calculated by Altshuler.² In the expression for $(\sigma_m^{av}(\epsilon))_{\text{correl}}$ the scattered amplitude is the coherent sum of amplitudes originating from individual scattering sites.

The structure factor $S(|\mathbf{q}|)$ is not known for CH_3OH gas. However, at low electron energies, i.e., in the long wavelength limit $|\mathbf{q}| \rightarrow 0$ the static structure factor can be approxi-

TABLE I. “Zero-field” density-normalized electron mobility $(\mu n)_0$ in CH_3OH , scattering cross section $\langle \sigma_m^{av}(\epsilon) \rangle^{\text{exp}}$, and second virial coefficient $B(T)$ of CH_3OH as a function of T (see the text).^a

T/K	$(\mu n)_0/10^{21} \text{ cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$	$\langle \sigma_m^{av}(\epsilon) \rangle^{\text{exp}}/10^{-13} \text{ cm}^2$	$B(T)/\text{cm}^3 \text{ mol}^{-1}$
303	4.28 ± 0.30	1.289 ± 0.090	-1228
333	4.45 ± 0.36	1.183 ± 0.095	-967
363	4.67 ± 0.33	1.080 ± 0.080	-607

^aThe errors are the maximum calculated errors determined by the method of error propagation. The standard deviation of the density normalized mobilities from the mean is $\leq 0.6\%$.

mated by $S(0) = nk_B T \chi_T$, where χ_T is the isothermal compressibility of the real polar gas (this limit is insensitive to orientational correlations of the dipole molecules). Just in the case $|\mathbf{q}| \rightarrow 0$ the total differential cross section diverges, but with the weighting factor $(1 - \cos \theta)$ in Eq. (7) which cuts the contributions from small angles (or large distances) the total momentum transfer cross section becomes finite. This cutting factor, however, is somewhat in contradiction to the limit $|\mathbf{q}| \rightarrow 0$ considered in the static structure factor. Nevertheless we take into account $S(0)$ as a rough estimate. Using the virial expansion with the second virial coefficient $B(T)$ one obtains approximately $S(0) \approx [1 + (2B(T)/N_A)n]^{-1}$, and Eq. (7) finally yields $(\sigma_m^{av}(\epsilon))_{\text{correl}} \approx \sigma_m^{av}(\epsilon) [1 + (2B(T)/N_A)n]^{-1}$ where N_A is Avogadro's constant and $B(T)$ is given in units of $\text{cm}^3 \text{ mol}^{-1}$. On the right hand side of Eq. (5) $\sigma_m^{av}(\epsilon)$ has to be substituted—in μ_L too—with $(\sigma_m^{av}(\epsilon))_{\text{correl}}$. Then one obtains for $\chi_T/L \ll 1$

$$\mu n \approx (\mu n)_0 \left(1 + (2B(T)/N_A)n - \frac{\pi^{1/2}}{8} \times (0.5\pi - 0.6)\chi_T \langle \sigma_m^{av}(\epsilon) \rangle^{\text{exp}} n + \dots \right), \quad (8)$$

where we have neglected a small term with n^3 .

In methanol gas for $T \geq 393 \text{ K}$ the calculated correction term due to coherent multiple scattering was relatively small in comparison with the second, incoherent contribution in Eq. (8) (see Fig. 7 in Ref. 7 and Fig. 4 of this work). Therefore, the measurements of the electron mobility in low density CH_3OH gas at lower temperatures are just the crucial tests in order to demonstrate convincingly that the first correction term in Eq. (8) is really significant—if not even dominating—at these low gas densities. This will be shown in the following analysis of the experimental results.

First of all we have to determine the experimental scattering cross sections $\langle \sigma_m^{av}(\epsilon) \rangle^{\text{exp}}$ in order to compare the “zero-field” density-normalized mobilities in low density CH_3OH with Polischuk's theoretical description. Therefore, we have extrapolated the dashed lines in Fig. 2 to $n \rightarrow 0$ to get $(\mu n)_0$ from which $\langle \sigma_m^{av}(\epsilon) \rangle^{\text{exp}}$ is obtained by using Eq. (6) (Table I). In addition we present in Fig. 3 $\langle \sigma_m^{av}(\epsilon) \rangle^{\text{exp}}$ as a function of the reciprocal temperature. Of course we have taken into account also the experimental results of Gee and Freeman.⁴ From their mean values $\mu n(T)$ for $300 \leq T \leq 617 \text{ K}$ (see the solid line in Fig. 5 of Ref. 4) we have calculated $\langle \sigma_m^{av}(\epsilon) \rangle^{\text{exp}}$ with the aid of Eq. (6). Moreover, we have used

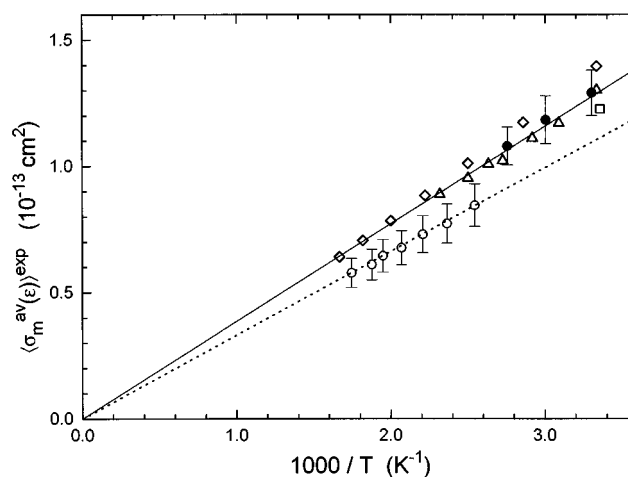


FIG. 3. The thermal averaged experimental momentum transfer cross section $\langle \sigma_m^{av}(\epsilon) \rangle^{\text{exp}}$ of methanol with respect to excess electrons vs the reciprocal temperature: \diamond , Gee and Freeman (Ref. 4); \triangle , Christophorou and Pittman (Ref. 14); \square , Ref. 18; \circ , Ref. 7; \bullet , this work. The error bars show the maximum calculated error (see the text and Table I). The solid line fits the data points \triangle , \bullet , and the high temperature data of Gee and Freeman. The pointed line represents the result of Altshuler (Eq. (4b) with $D = 1.70$ Debye).

most of the results of Christophorou and Pittman¹⁴ determined in CH_3OH at very low densities ($n < 4.6 \times 10^{18} \text{ cm}^{-3}$) applying again Eq. (6). For completeness we have drawn in Fig. 3 a scattering cross section obtained by Christophorou *et al.*¹⁸ in a diluted gas mixture of CH_3OH in ethylene. Finally we consider also our own results obtained by an extrapolation procedure from high density measurements.⁷

The scattering cross sections determined by us for $T \leq 363 \text{ K}$ agree very well with those of Christophorou and Pittman. For $T \leq 450 \text{ K}$ the results of Gee and Freeman show stronger deviations from our low temperature results. At higher temperatures their results obtained for $n = 2.9 \times 10^{18} \text{ cm}^{-3}$ join—as it is expected—the $1/T$ dependence of $\langle \sigma_m^{av}(\epsilon) \rangle^{\text{exp}}$ given by the solid line in Fig. 3 which fits the results of Christophorou and Pittman and our own results at lower temperatures. We notice, however, that the extrapolation of our high density measurements performed in a high pressure photocell yields scattering cross sections which are systematically too small by about 16%. The origin of this systematic underestimate is not known at present.¹⁹ It should be pointed out, however, that the essential conclusions drawn in Ref. 7 are not touched by this fact.

For comparison we have also calculated $\langle \sigma_m^{av}(\epsilon) \rangle^{\text{theor}}$ with Altshuler's Eq. (4b) (pointed line in Fig. 3). It follows that for the temperature range $300 \leq T \leq 600 \text{ K}$ $\langle \sigma_m^{av}(\epsilon) \rangle^{\text{exp}}$ is about 16% higher than the Born result for point dipoles and its temperature dependence can be reasonably described by $\langle \sigma_m^{av}(\epsilon) \rangle^{\text{exp}} = A' m_e / k_B T$ with $A' = 5.85 \text{ cm}^4 \text{ s}^{-2}$.

With this knowledge on $\langle \sigma_m^{av}(\epsilon) \rangle^{\text{exp}}$ as a function of T we can now calculate the quantum density correction due to the interference in multiple scattering. A sensitive representation of this correction obtained from Eq. (5) has the following form

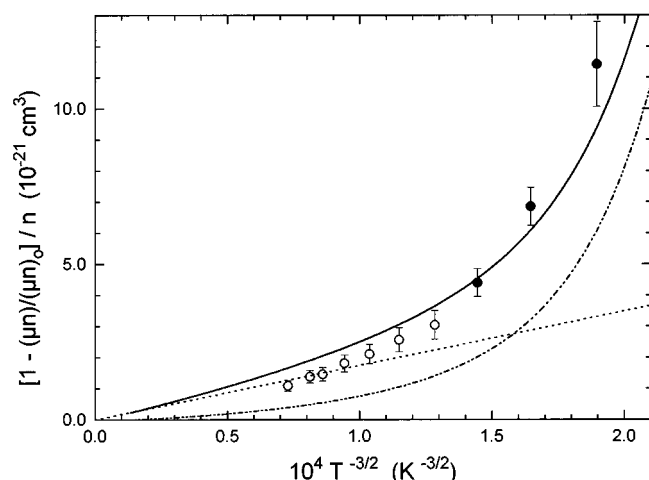


FIG. 4. Temperature dependence of the density corrections to the classical Lorentz mobility, Eq. (1): ●, experimental results for $303 \leq T \leq 363$ K; ○, experimental results for $393 \leq T \leq 573$ K; ·····, quantum density correction due to interference in multiple scattering, Eqs. (5) and (6); - · - · - ·, contribution $-2B(T)/N_A$ due to positional correlations among the scatterers; —, the sum of both effects obtained from Eq. (8).

$$[1 - (\mu n)/(\mu n)_0]/n = \frac{\pi^{1/2}}{8} (0.5\pi - 0.6) \chi_T \langle \sigma_m^{av}(\epsilon) \rangle^{\text{exp}} \propto T^{-3/2}. \quad (9)$$

The r.h.s. expression of Eq. (9) is proportional to $T^{-3/2}$ because we have just found out that the thermal average of the momentum transfer cross section depends on T^{-1} . Therefore, we have plotted in Fig. 4 the experimental value $[1 - (\mu n)/(\mu n)_0]/n$ against $T^{-3/2}$. The error bars at the experimental points represent the maximum calculated errors. The pointed line is given by the r.h.s. expression of Eq. (9). It follows that the quantum density correction due to the interference in multiple scattering does by far not describe the observed density dependence of (μn) in methanol at lower temperatures.

With the second virial coefficient $B(T)$ of CH_3OH from Ref. 10 (see also Table I) we have calculated the r.h.s. expression of Eq. (8) with the additional correction term $2B(T)n/N_A$. The sum of both corrections is presented as a solid line in Fig. 4 and shows now satisfactory agreement with experiment keeping in mind the numerous aforementioned approximations.

For the 303 K mobility isotherm we show explicitly the different density corrections in Fig. 5. At this “low” temperature the coherent multiple scattering contribution due to positional correlations among the scatterers is in fact predominating as suggested by us in Ref. 7.

IV. SUMMARY AND CONCLUDING REMARKS

We have found that the experimentally observed density and temperature dependence of the “zero-field” density-normalized electron mobility (μn) in the low density regime of CH_3OH gas can be described, at least qualitatively, by the quantum density correction due to interference in multiple

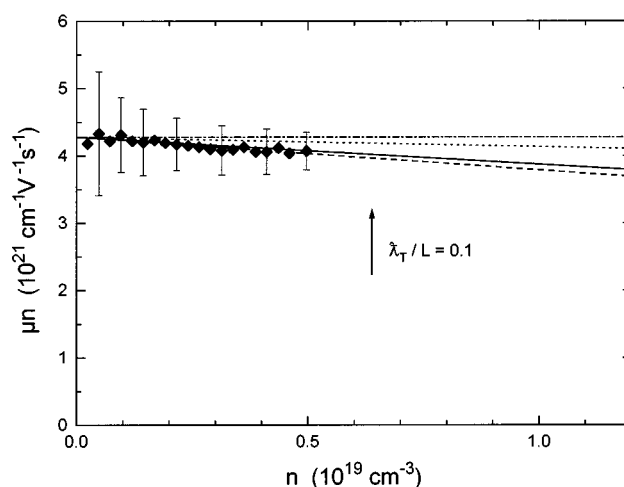


FIG. 5. Density corrections to the “zero-field” density-normalized mobility as a function of n : ◆, experimental results at $T = 303$ K (this work); —, linear regression; - · - · - ·, classical behavior, Eq. (1); ·····, interference in multiple scattering, Eqs. (5) and (6); —, interference in multiple scattering and correlations between the dipole scatterers, Eq. (8). The arrow signs the density where the de Broglie wavelength λ_T of thermal electrons is equal to one tenth of their mean free path L .

scattering and by the correlation (in position) among scatterers taken into account by the static structure factor $S(|\mathbf{q}| \approx 0)$. The analysis yields a thermal averaged momentum transfer cross section $\langle \sigma_m^{av}(\epsilon) \rangle^{\text{exp}}$ which is about 16% higher than that calculated with Altshuler’s Born approximation formula for point-dipoles.

To study the temperature dependence of $\langle \sigma_m^{av}(\epsilon) \rangle^{\text{exp}}$ in polar gases like CH_3OH in order to test for instance the generalized ansatz $\sigma_m^{av}(\epsilon) = A_\alpha / \epsilon^\alpha$ ($\alpha \neq 1$) it is necessary to perform temperature dependent mobility measurements at sufficiently low gas densities (where the variation of (μn) with n is much smaller than the experimental error). For future electron mobility measurements in other polar gases the meaning of “sufficiently low gas densities” must be checked in each case. From our investigation it follows that for electrons in CH_3OH the number density n must be as low as some 10^{17} cm^{-3} . However, when experiments are made at to some extent higher densities ($10^{18} - 10^{19} \text{ cm}^{-3}$) one has to single out the multiple scattering contributions to obtain finally the Lorentz limit of the electron mobility. In particular at lower temperatures positional correlations among the polar scatterers may play a dominating role. Therefore, it is not sufficient to perform mobility measurements at a few gas density values. The density and temperature dependence of (μn) should be studied rather systematically.

Within the experimental errors $\langle \sigma_m^{av}(\epsilon) \rangle^{\text{exp}}$ in CH_3OH shows a simple T^{-1} temperature dependence in the temperature range $300 \leq T \leq 600$ K. It seems to us that it would mean to overestimate the accuracy of the $\langle \sigma_m^{av}(\epsilon) \rangle^{\text{exp}}$ values if one uses $\sigma_m^{av}(\epsilon) = A_\alpha / \epsilon^\alpha$ ($\alpha \neq 1$) for a better description of the scattering cross section.

From this study we conclude further that the discussed multiple scattering effects play also an important role in the case of electrons in low density H₂O gas investigated by Gee and Freeman.⁴ The correction due to the static structure factor $S(|\mathbf{q}| \approx 0)$ is comparable to that in methanol because the second virial coefficient $B(T)$ is of the same order.²⁰ The experimental scattering cross section of H₂O ($D=1.85$ Debye), however, is almost twice as large as that calculated with Eq. (4b), i.e., $\langle \sigma_m^{av}(\epsilon) \rangle^{\text{exp}} = 2.367 \times 10^{-13} \text{ cm}^2$ at 300 K.¹⁴ Therefore, the quantum interference correction estimated from Eq. (9) for the density range $4.2 \times 10^{17} \leq n \leq 9.4 \times 10^{18} \text{ cm}^{-3}$ covered by the measurements of Gee and Freeman is by a factor of almost two larger in H₂O than in CH₃OH. The sum of both multiple scattering effects should be observed more easily in H₂O than in CH₃OH gas. Hence the averaging procedure used by Gee and Freeman is not allowed at all for electrons in H₂O.

Our former electron mobility results in the low density saturated H₂O vapor ($296 \leq T \leq 376 \text{ K}$)²¹ which agree with those of Gee and Freeman cannot be simply analyzed. On the one hand the approximation for the structure factor $S(\mathbf{q})$ cannot be used anymore on the other hand one has to consider both, correlations in position and correlations in orientation of the dipole molecules.²² However, up to now there exists no theoretical description of the quantum interference in multiple scattering taking into account orientational correlations.

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- ¹ See, e.g., L. G. Christophorou and A. A. Christodoulides, *J. Phys. B* **2**, 71 (1969).
- ² S. Altshuler, *Phys. Rev.* **107**, 114 (1957).
- ³ W. R. Garrett, *Mol. Phys.* **24**, 465 (1967).
- ⁴ N. Gee and G. R. Freeman, *Can. J. Chem.* **61**, 1664 (1983).
- ⁵ See, e.g., K. W. Schwarz, *Phys. Rev. B* **21**, 5125 (1980), and references therein.
- ⁶ See, e.g., V. M. Atrazhev and I. T. Iakubov, *J. Phys. D* **10**, 2155 (1977).
- ⁷ P. Krebs and U. Lang, *J. Phys. Chem.* **100**, 10 482 (1996).
- ⁸ Th. Klahn and P. Krebs, *Ber. Bunsenges. Phys. Chem.* **98**, 1630 (1994).
- ⁹ Th. Klahn and P. Krebs (to be submitted).
- ¹⁰ Thermodynamic Research Center 1972, *Selected Values of Properties of Chemical Compounds*, Texas A&M University, Vol. I, Table 23-18-2-(1.0213)-h.
- ¹¹ A. Ya. Polischuk, *J. Phys. B* **18**, 829 (1985), and references therein.
- ¹² A. A. Abrikosov, L. P. Gor'kov, and F. E. Dzyaloshinskii, *Methods of Quantum Field Theory in Statistical Physics* (Prentice-Hall, Englewood Cliffs, NJ, 1969).
- ¹³ J. L. Pack, R. F. Voshall, and A. V. Phelps, *Phys. Rev.* **127**, 2084 (1962).
- ¹⁴ L. G. Christophorou and D. Pittman, *J. Phys. B* **3**, 1252 (1970).
- ¹⁵ (a) P. Krebs and St. Vautrin, *J. Phys. IV (Paris), Colloq. C5, Suppl.* **1**, 115 (1991); (b) Th. Klahn, P. Krebs, and U. Lang, in *Proceedings of a NATO Advanced Study Institute on Linking the Gaseous and Condensed Phases of Matter: The Behavior of Slow Electrons*, edited by L. G. Christophorou, E. Illenberger, and W. F. Schmidt (Plenum, New York, 1994), p. 339.
- ¹⁶ L. Van Hove, *Phys. Rev.* **95**, 249 (1954).
- ¹⁷ (a) T. H. Davis, L. D. Schmidt, and R. M. Minday, *Phys. Rev. A* **3**, 1027 (1971); (b) J. Lekner, *Philos. Mag.* **18**, 1281 (1972); J. Lekner and A. R. Bishop, *ibid.* **27**, 297 (1973).
- ¹⁸ L. G. Christophorou, G. S. Hurst, and W. G. Hendrick, *J. Chem. Phys.* **45**, 1081 (1966).
- ¹⁹ The error bars for $\langle \sigma_m^{av}(\epsilon) \rangle^{\text{exp}}$ for $T \geq 393 \text{ K}$ in Fig. 3 are the maximum errors calculated by the method of error propagation with the *known* error sources. The systematic underestimate of $\langle \sigma_m^{av}(\epsilon) \rangle^{\text{exp}}$ corresponding to a systematic overestimate of (μn) in the order of 16% is "characteristic" for the lower density measurements because (μn) values for ions determined by us at much higher densities and higher temperatures agree to within 3% with those of Gee and Freeman (Ref. 4).
- ²⁰ J. P. McCullough, R. E. Pennington, and G. Waddington, *J. Am. Chem. Soc.* **74**, 4439 (1952).
- ²¹ V. Giraud and P. Krebs, *Chem. Phys. Lett.* **86**, 85 (1982).
- ²² See, e.g., J. P. Hansen and I. R. McDonald, *Theory of Simple Fluids*, 2nd ed. (Academic, London, 1990).