Excess electron mobility in low density CH$_3$CN gas: Short-lived dipole-bound electron ground states as precursors of localized electron states

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We measured the mobility of excess electrons in the strongly polar acetonitrile (CH$_3$CN) gas at low densities as a function of density and temperature by the pulsed Townsend method. We found an unexpected strong density dependence of the ''zero-field'' density-normalized mobility (μn) that cannot be explained only by different multiple-scattering effects. We propose a transport process where short-lived *dipole-bound electron ground states* as quasilocalized states are involved. Finally we discuss the experimentally observed anion mobilities as a function of density and temperature according to current theoretical approaches. [S1050-2947(97)04401-6]

I. INTRODUCTION

Slow electrons drifting under the influence of an external electric field E in polar gases undergo strong scattering due to the long-range anisotropic electron–electric-dipole interaction [1]. For polar gases with a dipole moment $D \approx 2$ D the number density n at which the de Broglie wavelength just exceeds the mean free path of the electron is low, i.e., in the order of some 10^{19} cm^{-3} at $T=300$ K. Therefore, multiple scattering has to be considered already at much lower densities. In addition, it cannot be excluded at all that the electron is temporarily or permanently captured by the dipole molecules forming molecular negative ions. The probability of such a process increases with n. Therefore, the electron mobility in polar gases may show a large dependence on n and T at these low densities.

Molecular negative ions formed by electron addition to closed-shell neutral molecules are frequently unstable relative to autodetachment. However, if the electric-dipole moment of the molecule is sufficiently large, then an electron may be captured in the electrostatic field of the molecule to form a so-called dipole-bound anion. It was Fermi and Teller [2] who first established the critical permanent electric-dipole moment $D_c=1.625$ D required to bind an electron.

Several authors [3–5] have shown that the electric-dipole field of a stationary molecule can bind an electron in an infinite number of bound states if D is greater than D_c. The electron exists in an extensive orbital, described by a diffuse wave function [6]. The consideration of rotational degrees of freedom in real molecular systems has a rather strong effect on the critical binding properties of polar molecules: the number of bound states of the electron in the dipolar field of a molecule with $D > D_c$ is reduced to a finite number [7]. However, the minimum dipole moment necessary to support at least *one* bound state is increased by 10 to 30 % in comparison with that of a dipole fixed in space. In this case D_c

depends on the effective dipole length, the rotational state, and the moments of inertia of the polar molecules [8].

The binding energies of dipole-bound electron states may be extremely small, at least in cases where the dipole moment is near the critical value. Thus, one could expect that the formation of the ''dipole-supported anion'' might be difficult to observe since the very diffuse and weakly bound electrons would be subject to stripping by thermal collisional processes within a gas sample and/or by the electric fields to which they are subjected in the process of mass analysis or in drift mobility measurements.

The dipole moment $D=3.925$ D of CH$_3$CN is far above D_c. By electron-impact experiments Stockdale *et al.* [9] observed the formation of (CH$_3$CN)$^-$ by capture of electrons from acetonitrile (or fragments of them) in highly excited Rydberg states. Sugiura and Arakawa [10] have also studied collisions of rare-gas atoms in excited Rydberg states with CH$_3$CN and in every case find evidence for production of (CH$_3$CN)$^-$ with a capture cross section $\sigma_R \approx 10^{-12}$ cm^{-2}. Compton and co-workers [9,11] failed, however, to detect the anion from direct thermal electron attachment in as warm experiment or *via* collisions of fast alkali atoms (whose electron is tightly bound in an s state) with CH$_3$CN.

It follows a period of cluster experiments. For instance (CH$_3$CN)$_m^-$ has been observed by collisional electron transfer to a distribution of CH$_3$CN clusters, including *monomers*, from high-Rydberg krypton atoms, but only with $m \geqslant 11$ [12]. This result seems to be in agreement with the small electron affinity E.A.$\approx 5 \times 10^{-4}$ eV of CH$_3$CN that has been determined by an *ab initio* calculation by Jordan and Wendoloski [13]. However, Hashemi and Illenberger [14] succeeded in observing dipole-supported (CH$_3$CN)$^-$ *via* a high-energy resonant attachment of free electrons to CH$_3$CN clusters followed by evaporations, although they cannot rule out the formation of radical anions of structural isomers of acetonitrile.

We are concerned with the electron-transport processes in *polar* gases, especially in the transition from the quasifree to the localized electron state. In the past we have performed extensive electron mobility measurements in subcritical and supercritical NH$_3$ [15,16] and subcritical H$_2$O [17] gas as a function of gas density and temperature up to very high den-

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sities in order to study this transition in a disordered medium of dipole scatterers. Then we continued these studies on electrons in subcritical and supercritical CH_3OH gas [18–20] and in subcritical CH_3CN gas [21] also at much lower densities to study multiple-scattering effects on the electron mobility. From the preliminary, and not very accurate results on the electron mobility in low-density saturated CH_3CN vapor, we suggested that we have found short-lived *dipole-bound electron ground states in thermal equilibrium* that are involved in the transport process [18]. We have also found some evidence for the formation of dipole-bound electrons in low-density HCN gas [22].

In the meantime we have performed electron mobility measurements in low-density CH_3CN gas with much higher accuracy. We want to present the results in this publication because Schermann and co-workers [23] have recently demonstrated that Compton's method for the production of $(CH_3CN)^-$ could be used as a general way to produce *ground-state* dipole-bound anions: Thermal electrons are attached to closed-shell polar molecules from laser-excited Rydberg atoms in a crossing-beam experiment where the single collision condition is fulfilled. Subsequently, Schermann and co-workers field detached the electron from the produced anion $(CH_3CN)^-$ to ensure that it possessed a weakly bound diffuse electron as expected for the dipole-bound species.

In contrast to the usually collision-free beam experiments in our swarm experiments, collisional relaxation and activation within thermodynamic equilibrium is operative. Therefore, it has become possible now to compare qualitatively nonequilibrium results of cluster experiments with thermal equilibrium results of mobility measurements in order to substantiate our idea.

In Sec. II we will give a short description of our experiments. The experimental results are presented and discussed in Sec. III. There we analyze the electron mobility observed in low-density CH_3CN gas according to Polischuk's theoretical calculations on quantum multiple-scattering corrections to the mobility of the electrons [24,25]. It will be demonstrated, at least qualitatively, that due to the real behavior of the dipolar gas, positional correlations between the dipole molecules cannot be neglected. All these effects, however, cannot describe the electron mobility as a function of gas density. In Sec. IV an effective electron localization process involving the dipole-bound state is proposed to take part in the electron transport. In Sec. V we discuss the measured anion mobilities according to current theoretical approaches. Conclusions are given in Sec. VI.

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_3CN gas by a short laser pulse (neodymium-doped yttrium aluminum garnet laser: $\lambda=266$ nm pulse duration <20 ns, and pulse energy <10 mJ, KrF excimer laser: $\lambda=248$ nm, pulse duration, <30 ns, and pulse energy <20 mJ). The swarm of about 10^4 to 10^6 electrons is drifting under the influence of an applied electric field E with the drift velocity ν_d giving rise to a constant induced current $i(t)$ through a load resistor
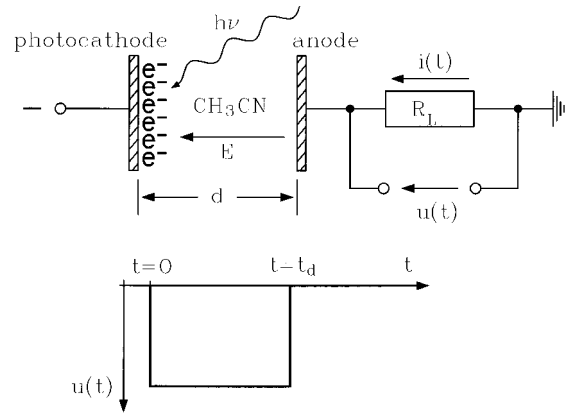

FIG. 1. Schematic diagram of the experimental setup of the time-resolved electron swarm technique (see the text).

R_L that drops to zero when all the electrons are collected by the anode at a distance d from the photocathode (see Fig. 1). The experimentally observed electron current pulse duration t_d in CH_3CN is in the order of 500 ns to 20 μs depending on E and the gas number density n. From the experimental linear relationship between $\nu_d=d/t_d$ and E, the mobility μ was determined from $\mu=\nu_d/E$ in the limit of zero field (see Fig. 2).

In connection with the electron mobility measurements in HCN we have developed a drift cell made out of Duran glas 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 ± 0.01 cm. This cell withstands pressures up to 40 bar for temperatures $T\leq400$ K [26]. Different pressure sensors can be coupled to the drift cell to measure the gas pressure in the drift space with an accuracy of ±0.6 mbar for the gas pressure range $p\leq200$ mbar and with ±2.5 mbar for $p\leq1$ bar.

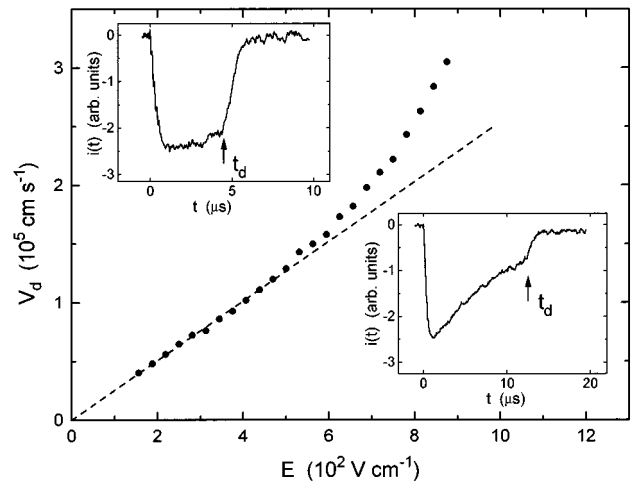The drift cell is also provided with a reservoir for about

FIG. 2. Experimentally observed drift velocity ν_d as a function of E for excess electrons in CH_3CN gas ($T=323$ K, $n=3.33\times10^{18}$ cm^{-3}). The insets show the recorded electron current waveforms for different electric field strengths. At low field strength (long drift time t_d) one can observe that a fraction of electrons is removed by attachment to CH_3CN forming *stable* anions (see Sec. V).

10 ml of CH_3CN purified by us in the following manner: Water-free acetonitrile (Aldrich, 99%) with a small amount of $NaBH_4$ (Merck, Sharp, and Dohme in Montreal, Canada) 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 1×10^{-6} mbar). The drift cell was then connected with the vacuum line in order to condense CH_3CN in the reservoir of the cell. Thereafter, CH_3CN 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 in addition that all parts of the apparatus that came in contact with CH_3CN, in particular the drift cell, are cleaned with several organic solvents and were finally rinsed with overheated water vapor for at least 10 h. The drift cell was then transfered into a steel tank filled with fine sand as a heat conducting medium. With an electrical heating system with proportional-integral-differential (PID) controllers (Eurotherm) the chosen temperature in the cell could be held constant to within ± 0.5 K. The temperature was controlled by NiCr-Ni thermocouples and by platinum thermoresistors Pt 100 that were mounted on different positions at the drift cell.

The gas pressure in the drift cell could be adjusted by careful opening of a valve connected with the vacuum line or by controlled filling of the empty cell. With the measured gas pressure and temperature the number density n of CH_3CN was determined from data in the literature [27]. We plan to publish further experimental details in Ref. [26].

III. RESULTS AND DISCUSSION

A. Experimental results

The electron mobility μ has been measured in the gas density range $1.2 \times 10^{17} \leq n \leq 7.2 \times 10^{18}$ cm^{-3} for the temperatures 303, 323, and 343 K. To give a survey on the experimental results we present in Fig. 3 the ''low-density'' mobility isotherms only for 303 and 323 K together with the ''high-density'' mobility isotherms for 368, 378, 388, and 398 K from Ref. [21]. We have omitted, however, the few inaccurate mobility data obtained by us in the low-density saturated vapor for $298 \leq T \leq 351.5$ K (see Refs. [18, 21]). Besides, we show also some anion mobility data mostly measured in the saturated CH_3CN vapor in the temperature range $314 \leq T \leq 389$ K.

By the variation of the number density n of CH_3CN by three orders of magnitude the electron mobility is changed by five orders of magnitude at these relatively low gas densities. At the highest CH_3CN gas density of this investigation, i.e., at $n = 7.2 \times 10^{19}$ cm^{-3} (398 K) the electron mobility has a value of 0.33 cm^2 V^{-1} s^{-1}. The mobility of anions (presumably $CH_3CN_{solv}^-$, see Sec. V) at this density is about 0.16 cm^2 V^{-1} s^{-1}. Obviously, the electron approaches a behavior that is reminiscent of heavy ions: therefore, the electrons should be almost completely quasilocalized. Quasilocalization means that even the most deeply localized electrons, whether they are trapped in density fluctuations, in cavities, or as negative ions, will have a finite mobility owing to diffusion of the gas molecules.
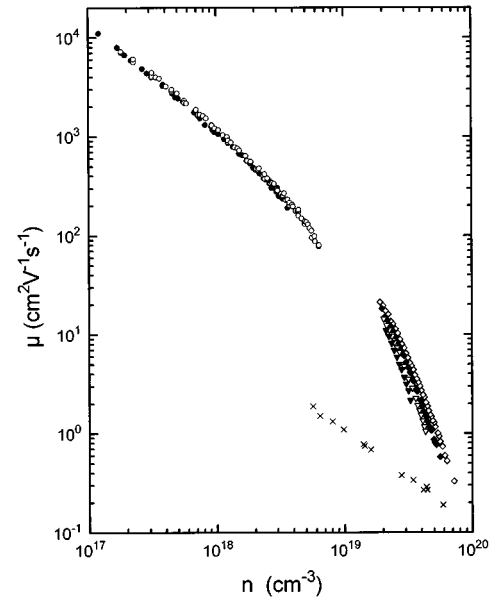

FIG. 3. Zero-field electron mobility in subcritical CH_3CN gas as a function of the gas number density n: ●, 303 K; ○, 323 K (the isotherm for $T = 343$ K has not been included in this figure; see, therefore, Fig. 5); ▼, 368 K; ▽, 378 K; ◆, 388 K; and ◇, 398 K. Anion mobilities in the saturated CH_3CN vapor: ×, $314 \leq T \leq 389$ K.

In the region where μ is strongly depressed by localization effects (see below) the drift velocity $v_d(E)$ exhibits a strongly nonlinear dependence on the electric-field strength E. The sensitivity of our present experimental setup did not allow us to reach the regime of linear response in the density range $n \geq 7.2 \times 10^{19}$ cm^{-3} ($T > 398$ K).

Taking a look first at the low-density mobility isotherms one notes a much stronger density dependence than the predicted classical $1/n$ behavior (see below). This striking effect
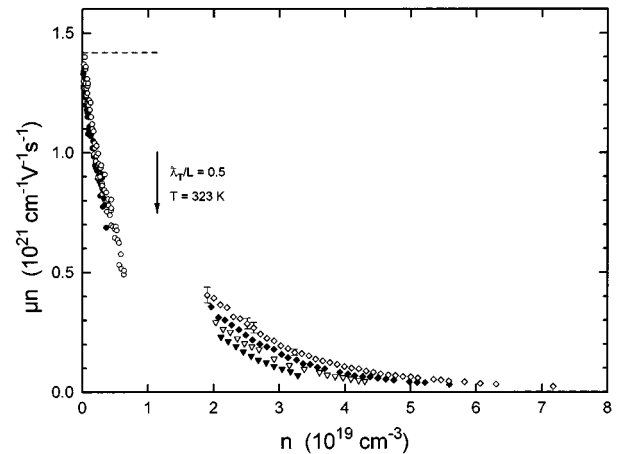

FIG. 4. Zero-field density-normalized mobility (μn) as a function of the gas number density n: ●, 303 K; ○, 323 K; ▼, 368 K; ▽, 378 K; ◆, 388 K; and ◇, 398 K. The error bars at some measured points give the maximum calculated error of $\pm$ 8%. The arrow signs the density, where the de Broglie wavelength λ_T of thermal electrons at $T = 323$ K is just half of their mean free path L. The dashed line shows the classical behavior of (μn) for $T = 323$ K.
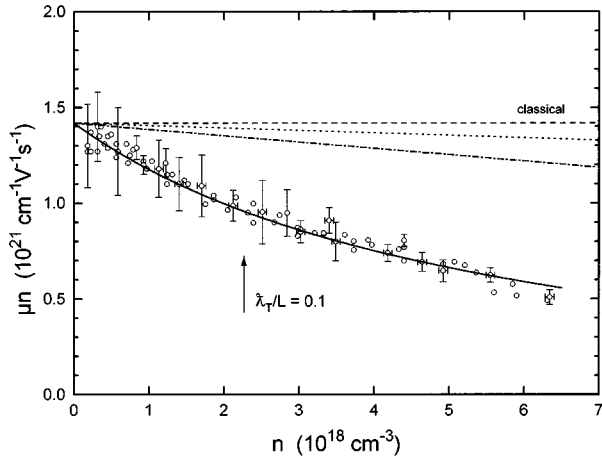
FIG. 5. ''Zero-field'' density-normalized electron mobility (μn) as a function of n at $T=323$ K: $\bigcirc$, experimental points. We have included only a few error bars. The different magnitudes of the error bars at about the same density are partially due to the different accuracies of the pressure sensors used in the drift experiment. $----$, classical behavior; $\cdots\cdots$, quantum density correction due to the interference in multiple scattering; $\cdot-\cdot-\cdot-\cdot$, Eq. (1), which in addition takes into account positional correlations between the dipole scatterers in the imperfect gas; and ———, Eqs. (5) and (6) considering the influence of dipole-bound electron ground states. The arrow signs the density for which the de Broglie wavelength $\lambdabar_T$ of thermal electrons becomes 1/10 th of their mean free path L.

is better visualized when the ''zero-field'' density-normalized mobility (μn) is shown as a function of n in a *linear* representation (see Fig. 4). For comparison, the classical behavior of the electron mobility is given by the horizontal dashed line.

The overall experimental uncertainties of (μn) at densities $n \geqslant 2 \times 10^{19}$ cm^{-3} was estimated to be $\pm 8\%$. Each low-density mobility isotherm has been measured several times up and down to show the reproducibility of these measurements. It is generally noticed that the scatter of the low-density data is relatively high (see also Fig. 5 with the maximum calculated errors shown at some arbitrarily selected experimental points). The origin for this is at present unknown. The observed extremely strong density variation of (μn) will be discussed in the following sections.

B. Multiple-scattering corrections

The ''zero-field'' density-normalized mobility (μn) of multiple scattered electrons in an imperfect polar gas is given by [19,20]

$$(\mu n) \approx (\mu_L n) \left\{ 1 - \frac{\sqrt{\pi}}{8} (0.5\pi - 0.6) \chi_T \langle \sigma_m^{\mathrm{av}}(\varepsilon) \rangle n \right.$$
$$\left. + \frac{2B(T)}{N_A} n \ldots \right\}, \tag{1}$$

where $(\mu_L n)$ is the classical density-normalized mobility in the single-collision approximation (Lorentz limit: see, e.g., Eq. (2) in Ref. [1]). The first density correction on the right-hand side of Eq. (1) is due to quantum interference in multiple scattering that has been calculated by Polischuk [24,25]. This term is valid only at sufficiently low gas densities where the de Broglie wavelength $\lambdabar_T = \hbar/(2m_e k_B T)^{1/2}$ of the thermal electrons is much smaller than their mean free path $L = 1/\langle \sigma_m^{\mathrm{av}}(\varepsilon) \rangle n$. $\langle \sigma_m^{\mathrm{av}}(\varepsilon) \rangle$ is the thermal average of the theoretical momentum-transfer cross section, $\sigma_m^{\mathrm{av}}(\varepsilon) = (4\pi/3)(De/\hbar)^2 m_e/\varepsilon$, for dipole molecules in the point-dipole limit averaged over the dipole orientations $[\varepsilon = (\hbar k)^2/2m_e$ is the kinetic energy of the electron] [28]:

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

The second correction term in Eq. (1) is due to positional correlations among the dipole scatterers in an imperfect gas that increases the single-event-scattering cross section via the structure factor $S(|\vec{q}|)$ [29,30]. At low energies $S(|\vec{q}|)$ can be approximated by its long wavelength limit $(|\vec{q}| \to 0)$, i.e., $S(0) = n k_B T \chi_T = \{1 + [2B(T)/N_A]n\}^{-1}$ where χ_T is the isothermal compressibility and $B(T)$ is the second virial coefficient (in units of cm^3 mol^{-1}) in a virial expansion of the equation of state of the imperfect gas.

The first-order theoretical calculations of Polischuk were only possible within the Born approximation (strictly speaking, for dipole molecules with $D < 2.5$ D). Since the experimental values of $\langle \sigma_m^{\mathrm{av}}(\varepsilon) \rangle$ in some media such as H$_2$O ($D = 1.85$ D) are almost twice as large as the Born ones [1], Polischuk proposed to use in Eq. (1) the thermally averaged experimental cross section $\langle \sigma_m^{\mathrm{av}}(\varepsilon) \rangle^{\mathrm{exp}}$ obtained from measurements at very low density [18–20]:

$$\langle \sigma_m^{\mathrm{av}}(\varepsilon) \rangle^{\mathrm{exp}} = \frac{8e}{3} (2/\pi m k_B T)^{1/2} [(\mu n)_0]^{-1}, \tag{3}$$

where $(\mu n)_0$ is the experimental ''zero-field'' density-normalized mobility in the limit of $n \to 0$. In this case $(\mu_L n)$ in Eq. (1) has to be replaced consequently by $(\mu n)_0$.

To compare the experimental results in CH$_3$CN gas with theory we display in Fig. 5, as an example, the ''zero-field'' density-normalized mobility (μn) vs n for $T=323$ K. The

TABLE I. $B(T)$, $(\mu n)_0$, $\langle \sigma_m^{\mathrm{av}}(\varepsilon) \rangle^{\mathrm{exp}}$, and K in CH$_3$CN gas as a function of T (see the text). The errors are standard rms errors given by the complete fitting procedure according to Eqs. (5) and (6) together with Eq. (1) (see below) using the maximum errors for (μn) and n calculated by the method of error propagation.

T (K)	$B(T)$ (cm^3 mol^{-1})	$(\mu n)_0$ (10^{21} cm^{-1} V^{-1} s^{-1})	$\langle \sigma_m^{\mathrm{av}}(\varepsilon) \rangle^{\mathrm{exp}}$ (Å^2)	K (10^{-19} cm^3)
303	-6543	1.340 ± 0.026	4118 ± 107	1.55 ± 0.12
323	-4299	1.419 ± 0.027	3766 ± 102	1.77 ± 0.10
343	-3038	1.476 ± 0.031	3514 ± 109	1.35 ± 0.13

dashed line is the classical result. The thermal averaged experimental scattering cross section is $\langle \sigma_m^{av}(\varepsilon) \rangle^{exp} = 3766 \pm 102$ Å^2 (see Table I), which is much smaller than $\langle \sigma_m^{av}(\varepsilon) \rangle^{theor} = 5469$ Å^2 obtained from Altshuler's Eq. (2). The experimental value $\langle \sigma_m^{av}(\varepsilon) \rangle^{exp} = 4118 \pm 107$ Å^2 for 303 K agrees quite well with 4359 Å^2 obtained by Christophorou and Christodoulides at 300 K.

One may argue that the Born approximation cannot be applied to molecules with $D > 2.5$ D. However, it is generally noticed that the relative difference between $\langle \sigma_m^{av}(\varepsilon) \rangle^{theor}$ and $\langle \sigma_m^{av}(\varepsilon) \rangle^{exp}$ is often much smaller for $D > 2.5$ D than for $D < 2.5$ D (see, e.g., electrons in H$_2$O at 300 K [1,16,17]: $\langle \sigma_m^{av}(\varepsilon) \rangle^{exp} \approx 2367$ Å^2 and $\langle \sigma_m^{av}(\varepsilon) \rangle^{theor} \approx 1303$ Å^2). This is also valid for electrons in CH$_3$CN: For $T = 300$ K one has $\langle \sigma_m^{av}(\varepsilon) \rangle^{theor} = 5888$ Å^2 and $\langle \sigma_m^{av}(\varepsilon) \rangle^{exp} = 4359$ Å^2. In our opinion this fact justifies afterwards the analysis according to Polischuk's theoretical calculations.

With the experimental scattering cross section one can calculate now the quantum density correction due to interference in multiple scattering [first correction term in Eq. (1)]. The result (pointed line in Fig. 5) shows that this is only a relatively small correction to the classical $(\mu n)_0$ in comparison with the experimentally observed strong density dependence of (μn). However, even at such low CH$_3$CN gas densities of the present investigation correlations between the scatterers cannot be neglected [19,20]. In a moderately dense polar gas one has to consider in principle both correlations in positions of the centers of mass and orientational correlations between the dipole molecules. Concerning the orientational correlation in CH$_3$CN it was found from dielectric polarization experiments performed by Buckingham and Raab [31] that for example at $T = 353$ K contributions from antiparallel orientations between neighboring molecular dipoles take part. Since there exists no theoretical description of the influence of orientational correlations of dipoles on multiple-scattering effects we take into account in the following only positional correlations. With $B(T = 323$ K$) = -4299$ cm^3 mol^{-1} (see Table I) one obtains from the complete Eq. (1) the dashed-dotted line presented in Fig. 5. That means that both density corrections in Eq. (1) are by far not sufficient to describe the density dependence of (μn) in CH$_3$CN, although Eq. (1) describes quite well the density dependence of (μn) in NH$_3$ gas ($D = 1.47$ D) in the large temperature range $300 \leq T \leq 650$ K [18] and in CH$_3$OH gas ($D = 1.70$ D) in the temperature range $303 \leq T \leq 573$ K [19,20], respectively. Therefore, it is concluded that there must exist a localization process that is more effective than the ''weak localization'' due to interference in multiple scattering. In Sec. IV we introduce a dynamical electron attachment-detachment equilibrium to describe the anomalous density dependence of the experimental (μn) in CH$_3$CN gas.

IV. THE DIPOLE-BOUND ELECTRON GROUND STATE AS A TEMPORARY LOCALIZATION CENTER

In this section we make use of a model on an oscillatory electron-transport process developed by Young [32] in order to describe in helium gas the transition from the quasifree to the localized electron state as a function of n. Therefore, it is necessary to recall a few fundamentals of this model including the adaption to the present problem.

The central assumptions in the following phenomenological considerations are

(i) In the imperfect CH$_3$CN gas there exist two unique electronic states, the *multiple scattered* quasifree electron state with mobility μ_f given by Eq. (1) and a quasilocalized state with the mobility μ_l.

(ii) Both states are characterized by thermodynamic lifetimes τ_{fl} and τ_{lf}, where τ_{fl} (τ_{lf}) is the characteristic decay time for the transition multiple scattered quasifree to quasilocalized (quasilocalized to multiple scattered quasifree) electron state.

In thermal equilibrium the lifetimes are related by $N_l^0 / \tau_{lf} = N_f^0 / \tau_{fl}$, where N_l^0 (N_f^0) is the equilibrium density of quasi-localized (multiple scattered quasifree) electrons. In the drift experiment the following process is considered: A single electron photoinjected at the phase boundary photocathode-CH$_3$CN gas drifts with a velocity $\mu_f E$ for a time of about τ_{fl} then forms a quasilocalized state and drifts for a time τ_{lf} with the velocity $\mu_l E$. Then it decays back to the multiple scattered state, etc. Young [32] has calculated the effective mobility μ^{eff} of the electron for such an oscillatory transport process that will continue until the electron arrives the anode. Assuming that the electron has been N times in the quasilocalized state he obtains

$$\mu^{eff} = \frac{(1 + 1/N) + (\mu_l / \mu_f)(\tau_{lf} / \tau_{fl})}{1 + (\tau_{lf} / \tau_{fl})} \, \mu_f. \qquad (4)$$

According to Young it is always possible to make E small enough so that the drift time t_d is much larger than the characteristic times τ_{fl} and τ_{lf} and therefore, $1/N \ll 1$. With the further assumption for the unknown μ_l that $\mu_l \ll \mu_f$ [and $(\tau_{lf} / \tau_{fl}) < (\mu_f / \mu_l)$] he finds the following approximation:

$$\mu^{eff} n = \frac{\mu_f n}{1 + (\tau_{lf} / \tau_{fl})}, \qquad (5)$$

where we identify now τ_{fl} and τ_{lf} with the corresponding *mean* characteristic times for the swarm of 10^4 to 10^6 electrons observed in our typical drift experiment.

Equation (5) shows clearly how the ''zero-field'' density-normalized mobility can be made to vary, as shown in Fig. 5 by varying τ_{lf} / τ_{fl}. It follows immediately that τ_{lf} / τ_{fl} must increase with increasing number density of the gas. Excellent agreement with experiment is found with the following relation linear in n (see the solid line in Fig. 5):

$$\tau_{lf} / \tau_{fl} = Kn \qquad (6)$$

with the constant $K = (1.77 \pm 0.10) \times 10^{-19}$ cm^3 for $T = 323$ K.

We now have to identify the quasilocalized electron state. For this purpose it seems to be more adequate to introduce the chemical language: The experimental result of Eq. (6) is in accordance with a dynamical electron attachment-detachment equilibrium

$$e_f^- + CH_3CN \overset{K}{\longleftrightarrow} (CH_3CN)_l^- \qquad (7)$$
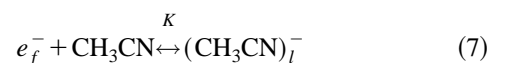
with the equilibrium constant $K = k_{fl} / k_{lf}$. The probability of the attachment of the multiple scattered electron to CH$_3$CN

depends on $k_{fl}n=1/\tau_{fl}$ and the electron detachment from the quasilocalized electron state $(CH_3CN)_l^-$ is given by the rate constant $k_{lf}=1/\tau_{lf}$ (τ_{lf} is the mean lifetime of the quasilocalized electron state).

If we assert now, as we have suggested recently [18], that $(CH_3CN)_l^-$ represents a dipole-bound electron ground state, then we have to show that the known properties of this state are in accordance with the conditions within the phenomenological model leading finally to Eq. (5).

(i) $\mu_l \ll \mu_f$. When the electron is coupled to the dipole molecule CH_3CN the self-diffusion coefficient of CH_3CN determines the mobility μ_l. However, neither the self-diffusion coefficient nor its density dependence is known at these low densities. Therefore, it seems to be reasonable to take the experimentally observed anion mobility as a rough measure for μ_l. From Fig. 3 it follows by extrapolation to low densities that $\mu_l \approx \mu_f/100$.

(ii) $t_d \gg \tau_{lf}, \tau_{fl}$. The experimentally observed drift time t_d should be by many orders of magnitude larger than the lifetimes τ_{lf}, τ_{fl}. Since the latter are related to the above-mentioned rate constants we can take, for instance, values for $k_{fl}=1/\tau_{fl}$ from literature. Mothes, Schultes, and Schindler [33] have determined the attachment rate constant k_{fl} by the electron-cyclotron resonance method, however, at much lower CH_3CN gas densities ($n \leq 10^{12}$ cm^{-3}) in comparison with those of our swarm experiment, without taking into account the possible detachment reaction they obtained for the disappearance of electrons $k_{fl}=7.2\times10^{-12}$ cm^3 s^{-1}. With this value we obtain from the equilibrium constant K, $\tau_{lf}=25$ ns, which is not sufficiently small in comparison with the observed drift time of several hundred nanoseconds to about 20 μs as required by the oscillatory model. Stockdale *et al.* [9] concluded from their swarm experiments that the attachment of thermal electrons to CH_3CN to form *stable* $(CH_3CN)^-$ is very small, if not zero. Their limiting value for the attachment rate constant was $k_{fl} \leq 1.24\times10^{-14}$ cm^3 s^{-1}. In this case the calculated $\tau_{lf}=14$ μs would be in total contradiction to the used model. However, as a precaution Stockdale *et al.* pointed out that the apparent inability of CH_3CN to attach thermal electrons may be due to an extremely short autoionization lifetime. In our opinion this means that k_{fl} may be several orders of magnitude larger than the above experimental estimate but the autodetachment rate constant (which can be lowered only by effective electronic to vibrational energy transfer) is also very high so that the formation of stable $(CH_3CN)^-$ could not be observed in their experiments performed at about 1.3 mbar CH_3CN. The lowest gas density of our investigation is 1.20×10^{17} cm^{-3} corresponding to 5 mbar (303 K). Under these conditions we do not observe any measurable influence of the dipole-bound state on the density-normalized mobility within the margins of the experimental error. On the basis of our experimental results Stockdale *et al.* did not have a chance to observe the attachment of thermal electrons in their swarm experiments.

Schermann and co-workers [23] studied charge-transfer collisions between laser-excited xenon (nf,np) Rydberg atoms, and acetonitrile molecules and clusters. $(CH_3CN)^-$ anions have been observed in these excellent supersonic expansion beam experiments (160 mbars of CH_3CN in 2 bars of rare gases) only in extremely narrow ranges of Rydberg n
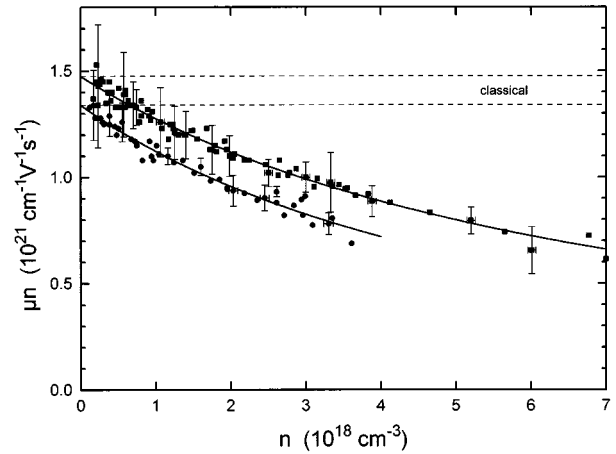

FIG. 6. ''Zero-field'' density-normalized electron mobility (μn) vs n: $\bullet$, 303 K; $\blacksquare$, 343 K; $----$, classical behavior; ———, Eqs. (5) and (6) with data from Table I (see the text and Fig. 5).

values. The attachment rate constant was found to be much higher, i.e., $k_{fl} \approx 10^{-8}$ cm^3 s^{-1} (the uncertainty was estimated to be $\pm 50\%$).

The idea of analogy of a Rydberg-excited electron with a slow ''free'' electron originated with Fermi [34]. Matsuzawa [35] has extended this analogy to examine ionization of a highly excited atom via collision with a polar molecule. The theoretical results of Matsuzawa [36] predict that the rate constant for the electron-transfer reaction will be equal to the thermal electron attachment rate constant. Therefore, we use the rate constant of Schermann and co-workers to interpret our experimental results. This attachment rate constant in the order of 10^{-8} cm^3 s^{-1} and the equilibrium constant $K=(1.77\pm0.10)\times10^{-19}$ cm^3 obtained in our swarm experiment yield $\tau_{lf} \approx 18$ ps and $\tau_{fl} \approx (1/n)\times10^{-10}$ s, where the number density n has to be substituted in units of 10^{18} cm^{-3}. These calculated lifetimes of the electron in the different states are, in fact, much smaller than the experimentally observed drift times between at least 400 ns and a few tens of microseconds in accordance with the conditions of the model.

(iii) The binding energy of the short-lived quasilocalized dipole-bound electron state: Such an oscillatory transport process with the short lifetime τ_{lf} due to the detachment process in the order of some tens of picoseconds is reasonable only if the binding energy of the quasilocalized electron is small, i.e., it should be comparable to the thermal energy.

The binding energy of $(CH_3CN)_l^-$ was determined by Schermann and co-workers by field detachment in the supersonic beam experiment. They obtained $E_b=-11.5$ meV [23]. This means that in our experiment the mean-thermal energy $(3/2)k_BT$ is more than three times larger than $|E_b|$ for the temperature range $303 \leq T \leq 343$ K.

In principle it is possible to get the free reaction energy for the reaction Eq. (7) from the temperature dependence of the equilibrium constant K. Therefore, in Fig. 6 we present, in addition, the experimental results for 303 and 343 K together with the corresponding fitting curves [Eqs. (5) and (6) using Eq. (1)]. The relevant parameters are collected in Table I. From the results for 303 and 343 K one can realize a decrease of K with increasing temperature (as it is expected). However, taking into account the deviating result for 323 K

in this temperature sequence and the standard rms error for K of at least $\pm 10\%$ it is more realistic at present to say that the equilibrium constant has a mean value of $\bar{K} \approx (1.56 \pm 0.25) \times 10^{-19}$ cm^3 for $303 \leqslant T \leqslant 343$ K. To get more information on the temperature dependence of K the mobility measurements have to be extended carefully to higher temperatures.

The proposed electron-transport process with the temporary nondissociative dipole-binding of an electron by CH$_3$CN is valid only in the gas-density range where $\lambda_T \ll L$. Concerning the multiple-scattering effects the comparison between theory and experiment shows in the case of NH$_3$ [18] and CH$_3$OH [19] that agreement is observed also at densities where $\lambda_T \approx L$, i.e., far beyond the validity range of the theory. Therefore, we conclude that the dipole-bound electron state is the precursor of the quasilocalized electron state observed at $n \leqslant 10^{20}$ cm^{-3}, where the electron mobility becomes comparable to the anion mobility (see Sec. V). Electron localization due to collective binding in a dense fluid (in clusters or in the bulk phase) should become dominating at liquid densities, i.e., at $n_{\text{liquid}}(\text{CH}_3\text{CN}) = 1.15 \times 10^{22}$ cm^{-3} ($T = 293$ K). In a pulse radiolytic study in *liquid* CH$_3$CN at 293 K Bell, Rodgers, and Burrows [37], have observed an absorption in the near IR region, the asymmetric broad shape of which is similar to those of solvated electrons. However, from numerous arguments the authors concluded that the absorbing species that is formed within 20 ns by electron capture is rather the solvated anion monomer (CH$_3$CN$^-$)$_{\text{solv}}$ that is in equilibrium with the solvated anion dimer $[(\text{CH}_3\text{CN})_2^-]_{\text{solv}}$.

V. ANION MOBILITY IN CH$_3$CN

A. Experimental results

At sufficiently high CH$_3$CN gas densities the recorded induced current is seen to have not only a fast component due to electrons but also a *slow* component, from which the time-of-flight t_d and finally the mobility of the slowly drifting species can be determined. From the low-field insert in Fig. 2 it follows that there is obviously a large probability for the electron to become *permanently* captured by CH$_3$CN molecules or by CH$_3$CN clusters in the (almost) saturated vapor. The slowly moving anions coexist with the quasilocalized electrons (see Fig. 3). In principle we can write down the following equation of formation

$$e^- + (\text{CH}_3\text{CN})_j \leftrightarrow (\text{CH}_3\text{CN})_j^- \quad \text{with} \quad j \geqslant 2, \quad (8)$$

where $(\text{CH}_3\text{CN})_j^-$ represents a negatively charged acetonitrile cluster consisting of j molecules.

The results of the few anion mobility measurements mostly performed in the saturated vapor are presented in Fig. 7 for the density range $5.65 \times 10^{18} \leqslant n \leqslant 5.86 \times 10^{19}$ cm^{-3} and for the temperature range $314 \leqslant T \leqslant 389$ K. Due to the increase of the temperature of the saturated vapour when going from low to high densities one observes a positive deviation from the usual $1/n$ dependence (compare the solid line with the pointed line in Fig. 7).
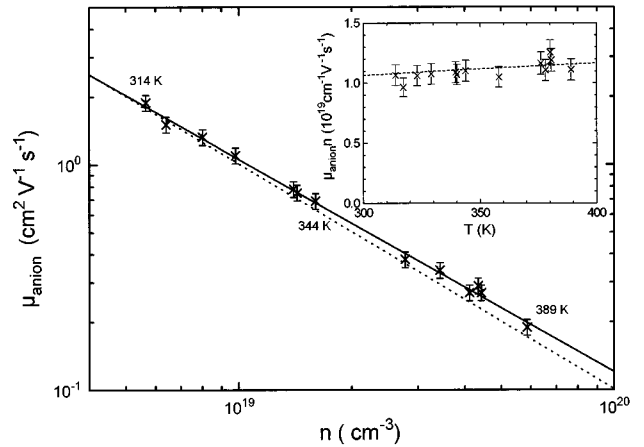

FIG. 7. Anion mobilities mostly measured in the saturated CH$_3$CN vapor as a function of n ($314 \leqslant T \leqslant 389$ K): $\times$, experimental points (the error bars show the estimated overall experimental uncertainty); ———, guide for the eyes; and $\cdots\cdots$, $1/n$ density dependence. The inset shows the density-normalized mobility ($\mu_{\text{anion}} n$) of anions as a function of temperature: $----$, theoretical approach of Su and Bowers given by Eq. (13) with $M_r \approx M$ (j is large).

B. Comparison between experiment and theory

It is not the aim of this section to mention all the different theoretical approaches published in the literature in order to describe the anion mobility in CH$_3$CN vapor. We rather focus on some relevant models. Publications concerned with ion-molecule collision rates have drawn attention to the relationship between the mobility of an ion and its collision frequency ξ for momentum transfer to the neutral molecule of the gas through which the ion moves. One has [38,39]

$$\mu_{\text{ion}} = e/m\xi, \quad (9)$$

where m is the ion mass and e a unit electron charge. To a good approximation ξ is given by

$$\xi = nk_c M(M+m)^{-1} \quad (10)$$

in which nk_c is the orbiting collision frequency of ion-molecule reaction rate theory, and M is the molecular mass of the neutral.

For a polar gas the ion is modeled with a point charge (e) and the neutral with a point dipole D embedded in a polarizable sphere with a mean polarizability α. Neglecting hard sphere or $1/r^{12}$ repulsive interactions the interaction potential between the ion and the neutral is then given by

$$V(r) = -\frac{\alpha e^2}{2r^4} - \frac{eD \cos\Theta}{r^2}, \quad (11)$$

where Θ is the angle between the direction of the dipole and the ion-dipole vector $\vec{r}$ ($|\vec{r}| = r$ is the charge dipole separation).

Su and Bowers [40] started with an r-dependent average orientation angle $\langle \Theta \rangle$ and have calculated values of a parameter C varying between zero and unity that allows for the effectiveness of the ''locking in'' of the dipole to the charge of the ion. The quantity k_c and the ion mobility are of the form

$$k_c = \frac{2\pi e}{M_r^{1/2}} \{ \alpha^{1/2} + CD(2/\pi k_B T)^{1/2} \}, \qquad (12)$$

$$\mu_{\text{ion}} = \{ 2\pi n M_r^{1/2} [\alpha^{1/2} + CD(2/\pi k_B T)^{1/2}] \}^{-1}, \qquad (13)$$

where M_r is the reduced mass of the system ion-neutral molecule. $C=1$ describes the so-called ''locked dipole'' case where the rotational motion of the neutral is neglected assuming that the approaching ion and the dipole are locked in the lowest energy configuration. Su and Bowers have calculated C as a function of $D/\alpha^{1/2}$ for $T=300$ K up to values of 1.732 D Å$^{-3/2}$. In the case of CH_3CN with $D/\alpha^{1/2}=1.859$ D Å$^{-3/2}$ (using $\alpha = 4.46$ Å^3 from Ref. [41]) one obtains by extrapolation $C=0.255$. The reduced mass is given by $M_r = Mj/(1+j)$, where j is the number of CH_3CN molecules forming the stable anion [see Eq. (8)]. Best agreement between theory and experiment is obtained for large j where $M_r \approx M$: $(\mu_{\text{anion}}n)^{\text{theor}} = 1.08 \times 10^{19}$ cm^{-1} V^{-1} s^{-1} for 300 K has to be compared with $(\mu_{\text{anion}}n)^{\text{exp}} = (1.07 \pm 0.09) \times 10^{19}$ cm^{-1} V^{-1} s^{-1} for 314 K. Assuming that the C value for 300 K is approximately valid also at 389 K one obtains from Eq. (13) a temperature dependence of $(\mu_{\text{anion}}n)^{\text{theor}}$ that is given by the dashed line in the inset of Fig. 7. The agreement between theory and experiment is excellent.

Nevertheless, the anion mobilities should be compared also with the results of Barker and Ridge [42] who used in their calculations another averaging procedure. Instead of averaging over the angle Θ, they calculate the average interaction energy for a statistical ensemble of ion-neutral pairs that leads finally to

$$V(r) = -\frac{\alpha e^2}{2r^4} - \frac{De}{r^2} \bar{L} \left(\frac{De}{r^2 k_B T_R} \right) \qquad (14)$$

instead of Eq. (11). The Langevin function $\bar{L}$ goes from zero to one as its argument goes from zero to infinity. Thus as the neutral rotational temperature T_R approaches zero or the dipole moment becomes large Eq. (14) approaches the ''locked dipole'' case. It was shown by Barker and Ridge that the momentum-transfer collision frequency ξ that determines μ_{ion} depends only on $D/\alpha^{1/2}$, on T_R, and on the translational temperature T. Numerical calculations on $k_c (M_r/\alpha)^{1/2}$ and on $(\xi/n)(m/(M_r \alpha)^{1/2})$ have been performed by the authors for the parameter range $0 \leq D/\alpha^{1/2} \leq 2.0$ D Å$^{-3/2}$ for $T = T_R = 300$ K (see Fig. 1 of Ref. [42]). Neglecting the small temperature difference between our experiment and theory

one obtains from these data in the limit of large j, $(\mu_{\text{anion}}n)^{\text{theor}} \approx 5.02 \times 10^{18}$ cm^{-1} V^{-1} s^{-1} which is only half of the experimental value $(\mu_{\text{anion}}n)^{\text{exp}} = (1.07 \pm 0.09) \times 10^{19}$ cm^{-1} V^{-1} s^{-1} at $T=314$ K. Obviously, the theoretical ansatz of Barker and Ridge underestimates the anion mobility in CH_3CN.

From the work of Su and Bowers it follows that the observed anions in CH_3CN are clustered (j is large). Disregarding the small temperature effect the density-normalized anion mobility does not decrease with increasing saturated vapor density due to further addition of CH_3CN molecules to the anion (see inset of Fig. 6). Therefore, we conclude that we observe, in fact, strongly clustered anions. In contrast to this we will report in Ref. [26] on an anomalous density dependence of anions in low-density HCN that are formed by (dissociative) electron addition to HCN.

VI. CONCLUSIONS

We have measured electron and anion mobilities in a wide range of densities and temperatures. The electron data have been analyzed carefully at those densities where the de Broglie wavelength is much smaller than the mean-free path of thermal electrons. The density dependence of the density-normalized mobility can be explained neither by interference in multiple scattering nor by correlations among the dipole scatterers in the imperfect gas. We have argued that dipole-bound electron ground states where the electron is ''localized'' for some tens of picoseconds in the dipole field of the slowly moving polar CH_3CN molecule influence the transport process. Although there exists no theoretical description of the electron mobility beyond those densities for which $\lambda_T/L \ll 1$ we conclude that the dipole-bound electron ground state $(CH_3CN)_1^-$ is the precursor of the quasilocalized electron state observed by the low mobilities at the high-density limit of this investigation. This quasilocalized electron state differs clearly from the anionic state $(CH_3CN)_j^-$ that is formed by electron capture by a CH_3CN cluster.

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