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**MOBILITY OF EXCESS ELECTRONS IN ACETONITRILE VAPOUR AND MULTIPLE SCATTERING PROCESSES IN DENSE POLAR VAPOURS**

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**Abstract** - Electron mobilities in acetonitrile vapour are reported for the temperature range  $298 \leq T \leq 398$  K up to vapour densities of about  $7 \times 10^{19} \text{ cm}^{-3}$  which show very strong deviations from the Lorentz behaviour. These results and those of electrons in other polar gases can be partially explained by density corrections of quantum character proposed by Polischuk.

**1. Introduction**

Since many years we are interested in the electron localization process in disordered polar media. Especially we want to know what is the influence of the long-range anisotropic electron-dipole interaction potential on the density dependence of the electron mobility. Therefore we have measured in the past the electron mobility in sub- and supercritical polar gases like  $\text{NH}_3$  /1, 2/ and  $\text{H}_2\text{O}$  /2, 3/ up to very high densities: in ammonia up to two times the critical density /4/. With regard to the problem of electron localization at that time these results could be discussed only qualitatively using arguments from solid-state physics like the Ioffe-Regel criterion /5/.

Recently, theoretical calculations by Polischuk on electrons in polar media /6/ have shown that the inclusion of interference in multiple scattering results in a density correction to the mobility and leads to its decrease with increasing vapour density in comparison with the results following from the Lorentz formula. It is this interference effect which is finally responsible for the electron localization at higher vapour densities.

It was pointed out by Polischuk that in the case of long-range interaction a new mechanism of quantum corrections to mobility may become effective which is due to changes in the law of electron dispersion /7/.

To study both quantum corrections to the electron mobility in moderately dense polar gases it would be interesting to determine the density dependence of the electron mobility in a system of dipole scatterers with a very high dipole moment like acetonitrile ( $\text{CH}_3\text{CN}$ ) which has a gaseous dipole moment of 3.96 Debye .

Preliminary results have been published already /8/. In this paper we present now electron mobility data in the temperature range  $298 \leq T \leq 398$  K and in the density range  $1.14 \times 10^{18} \leq$

$n \leq 7,17 \times 10^{19} \text{ cm}^{-3}$ . These results are discussed in detail.

## 2. Experimental

The mobility of electrons was measured by a time of flight method. Electrons were photoinjected from a stainless-steel or silver photocathode into  $\text{CH}_3\text{CN}$  vapour by a short excimer laser pulse (Kr/F: wavelength 249 nm, pulse duration 25 ns). The electrons are drifting in an applied electric field  $E$  with the drift velocity  $v_d$  giving rise to a photocurrent which drops to zero after a time  $t_d$  when all the electrons are collected by the counter electrode at a distance  $d$  (0.5 to 2 mm) from the photocathode. From the experimental linear relationship between  $v_d = d/t_d$  and the electric field strength  $E$  the mobility was determined from  $\mu = v_d/E$  as a function of acetonitrile vapour number density  $n$ . The determination of  $n$  and the purification of  $\text{CH}_3\text{CN}$  are described in our preliminary report /8/. For experimental details concerning the high pressure photocell we refer to the work of Krebs and Wanschik /9/.

## 3. Results and Discussion

First of all it must be pointed out that the lifetime of the photoinjected electrons in  $\text{CH}_3\text{CN}$  is much longer (sometimes by many orders of magnitude) than those reported in (or calculated from) the literature /10/.

For two reasons the electron mobility measurements were rather difficult:

- (i) In the region where  $\mu$  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 set-up did not allow to reach the regime of linear response in the density range  $n > 7.17 \times 10^{19} \text{ cm}^{-3}$  ( $T > 398 \text{ K}$ ).
- (ii) Sometimes acetonitrile condensed on the photocathode surface. Photoinjected electrons were scavenged at least partially. In this case we did not observe the usual photocurrent pulses:  $t_d$  could not be determined.

The results of the mobility measurements are shown in figure 1. There we have plotted the so-called density-normalized mobility  $\mu \cdot n$  versus  $n$  in comparison with some selected results for electrons in  $\text{H}_2\text{O}$  and  $\text{NH}_3$  /2/.

The density-normalized mobility  $\mu n$  of electrons in  $\text{CH}_3\text{CN}$  is lower than that in  $\text{H}_2\text{O}$  vapour and even more markedly lower than  $\mu n$  in  $\text{NH}_3$  gas. In comparison with  $e^-$  in  $\text{H}_2\text{O}$  and  $\text{NH}_3$  deviations from the Lorentz behaviour ( $\mu_L n = \text{const}_n$ ) are observed at much lower densities ( $n \simeq 4 \times 10^{18} \text{ cm}^{-3}$ ).

At very low vapour densities the mobility of quasi-free electrons is given by the so-called Lorentz limit /11/

$$\mu_L = - \frac{4\pi}{3} \frac{e}{m} \frac{1}{n} \int_0^{\infty} \frac{v^2}{\sigma_m(v)} \frac{df_0}{dv} dv \quad (1)$$

where  $\sigma_m(v)$  is the momentum transfer cross section for the scattering of the electrons by an isolated molecule as a function of the relative electron velocity  $v$ . The electron velocity distribution function is given by

$$f_0(v) = (m/2\pi k_B T)^{3/2} \exp(-mv^2/2k_B T). \quad (2)$$

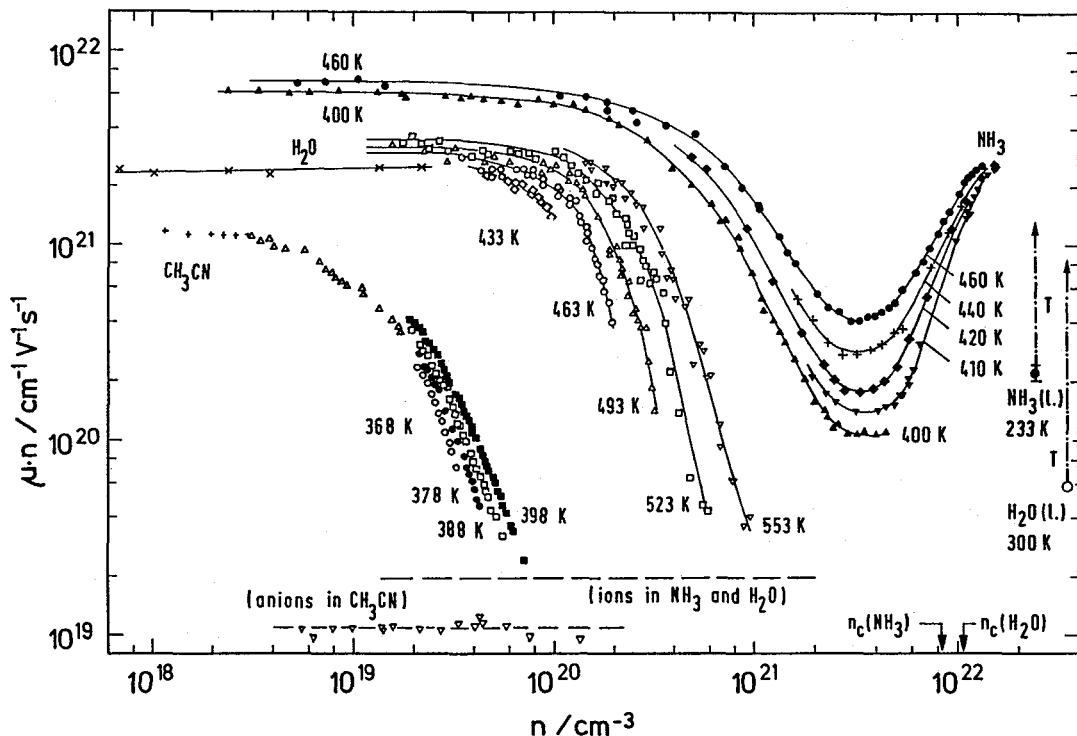


Fig.1 Plot of the density-normalized mobility  $\mu n$  of electrons in  $\text{CH}_3\text{CN}$ ,  $\text{H}_2\text{O}$  and  $\text{NH}_3$  vapour, respectively, versus number density  $n$  for several temperatures.  $\text{CH}_3\text{CN}$ : +, 298 K;  $\Delta$ , saturated  $\text{CH}_3\text{CN}$  vapour ( $298 \leq T \leq 351.5$  K); o, 368 K;  $\bullet$ , 378 K;  $\square$ , 388 K;  $\blacksquare$ , 398 K;  $\nabla$ , anions in  $\text{CH}_3\text{CN}$  ( $314 \leq T \leq 470$  K).  $\text{H}_2\text{O}$ :  $\diamond$ , 433 K; o, 463 K;  $\Delta$ , 493 K;  $\square$ , 523 K;  $\nabla$ , 553 K; x, saturated  $\text{H}_2\text{O}$  vapour ( $296 \leq T \leq 376$  K) /2, 3/.  $\text{NH}_3$ :  $\blacktriangle$ , 400 K;  $\blacktriangledown$ , 410 K;  $\blacklozenge$ , 420 K; +, 440 K;  $\bullet$ , 460 K /2/. The solid lines are intended as guides for the eye. The dashed line represents the density-normalized mobility of cations in  $\text{NH}_3$  and  $\text{H}_2\text{O}$  vapour. On the high density side the mobilities of excess electrons in liquid  $\text{NH}_3$  ( $T = 233$  K) and liquid  $\text{H}_2\text{O}$  ( $T = 300$  K) have been included. The lines  $\dashrightarrow$  show the expected shift of these mobilities for the corresponding high temperatures.

For dipole molecules (in the point-dipole approximation) the momentum transfer cross section  $\sigma_m(v)$  within the Born approximation takes the form /12/

$$\sigma_m(v) = A/v^2 \quad \text{with} \quad A = \frac{8\pi}{3} (De/\hbar)^2 \quad (3)$$

where  $D$  is the dipole moment of the scatterers. In the binary collision approximation (equation (1)) the transport collision frequency is given by

$$\tilde{\nu}_m^0 = \sigma_m(v) v n \quad (4)$$

Taking into account the interference effects in multiple scattering the collision frequency is increased in comparison with  $\tilde{\nu}_m^0$ . One has /6/

$$\tilde{\nu}_m = \tilde{\nu}_m^0 [1 + (0.5\pi - 0.6)\hbar \sigma_m(v) n / mv] \quad (5)$$

which due to  $\hbar$  shows the quantum nature of this density correction. Finally the following deviation from the Lorentz limit  $\mu_L$  is obtained /6,13/

$$\mu / \mu_L = 1 - \frac{\sqrt{\pi}}{8} (0.5\pi - 0.6) \hbar \frac{\langle \sigma_m(v) \rangle}{(2mk_B T)^{1/2}} n \quad (6)$$

$$\text{with } \langle \sigma_m(v) \rangle \equiv 4\pi \int_0^\infty \sigma_m(v) f_0(v) v^2 dv = Am/k_B T$$

which is valid, however, only for  $\lambda/L \ll 1$ , where  $\lambda = \hbar/(2mk_B T)^{1/2}$  and  $L = 1/n \langle \sigma_m(v) \rangle$  are the de Broglie wavelength and the mean free path of the electrons, respectively.

It should be pointed out that equation (6) differs from that given by Polischuk. The original formula has been corrected by us in order to take into account the above defined mean scattering cross section /13/.

The theoretical calculation was only possible within the Born approximation, i.e. for molecules with a dipole moment much smaller than 2.5 Debye. In the case of  $\text{NH}_3$  ( $D = 1.47$  Debye) and  $\text{H}_2\text{O}$  ( $D = 1.85$  Debye) the experimental cross sections  $\langle \sigma_m(v) \rangle^{\text{exp}}$  are about twice as large as the corresponding Born cross sections (see e.g. /2/). Therefore, Polischuk proposed to use in equation (6) the averaged cross section  $\langle \sigma_m(v) \rangle^{\text{exp}}$  obtained from low-density measurements:

$$\langle \sigma_m(v) \rangle^{\text{exp}} = \frac{8e}{3} \left( \frac{2}{\pi m k_B T} \right)^{1/2} \frac{1}{(\mu n)_0} \quad (7)$$

where  $(\mu n)_0$  is the experimental density-normalized electron mobility at low vapour densities.

We have analysed electron mobility data in  $\text{NH}_3$  and  $\text{H}_2\text{O}$  in this context /13/. Using also the data of Christophorou et al. /14/ we could show that for electrons in  $\text{NH}_3$  we obtain an excellent agreement between equation (6) and the experimental results in the temperature range  $300 \leq T \leq 650$  K. An example is given in figure 2. Obviously, the interference in the processes of multiple scattering describes the experimentally observed drop of the electron mobility with increasing vapour density. It is generally noted that in spite of the fact that the theoretical description is only valid for vapour densities where  $\lambda/L \ll 1$  (i.e. for  $n \ll 1/(\lambda \cdot \langle \sigma_m(v) \rangle)$ ) agreement between theory and experiment is observed in a much larger density range /13/.

Due to its high dipole moment the Born approximation should not be valid for  $\text{CH}_3\text{CN}$ . From the Lorentz limit we have determined for  $T = 298$  K the mean scattering cross section  $\langle \sigma_m(v) \rangle^{\text{exp}} = 4888 \pm 390 \text{ \AA}^2$  which compares well with  $\langle \sigma_m(v) \rangle^{\text{exp}} = 4359 \text{ \AA}^2$  determined by Christophorou et al. /15/. From equation (3) one obtains within the Born approximation  $\langle \sigma_m(v) \rangle^{\text{theor}} = 5972 \text{ \AA}^2$  /15/. Obviously, in the case of  $\text{CH}_3\text{CN}$  the Born approximation point-dipole calculation of Altshuler shows smaller deviations from  $\langle \sigma_m(v) \rangle^{\text{exp}}$  compared to  $\text{NH}_3$  and  $\text{H}_2\text{O}$ . This fact

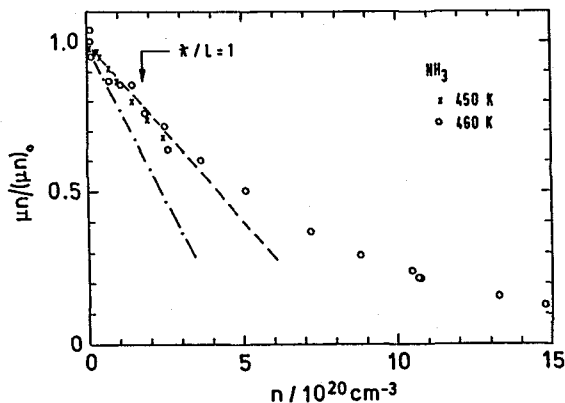


Fig. 2 Comparison of the experimental density-normalized mobility  $\mu n/(\mu n)_0$  as a function of density for electrons in  $\text{NH}_3$  with the theoretical calculations. Experiment: x,  $T = 450 \text{ K}$  /14/; o,  $T = 460 \text{ K}$  /2, 13/. Theory: ---, equation (6); -·-·-, equation (8);  $T = 460 \text{ K}$ ,  $\langle \sigma_m(v) \rangle^{\text{exp}} = 568 \text{ \AA}^2$ .

justifies an analysis of the electron mobility data according to Polischuk's theory (equ. (6)) including a further density correction of quantum character to the mobility which is associated with the change in the sign of the electron dispersion /7,13/.

$$\mu/\mu_L = 1 - \frac{(4 - \pi)\sqrt{\pi}}{4} \frac{\langle \sigma_m(v) \rangle}{\hbar (2mk_B T)^{1/2}} n \quad (8)$$

The results of this analysis are presented in figure 3. For the calculations according to

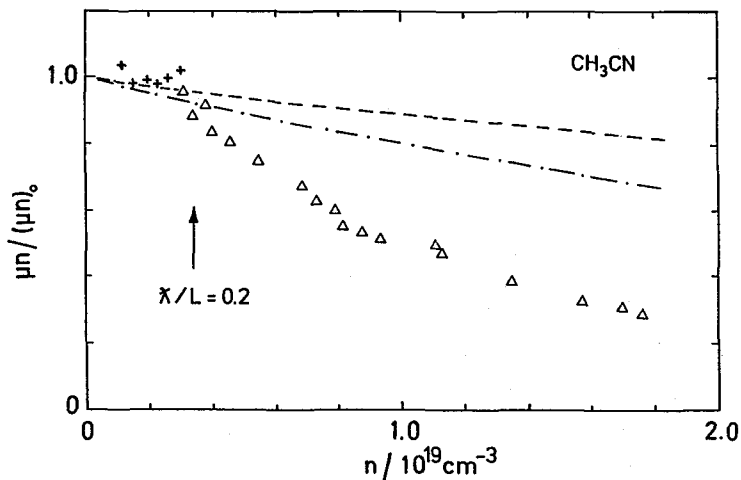


Fig. 3 Comparison of the experimental density-normalized mobility  $\mu n/(\mu n)_0$  as a function of density for electrons in  $\text{CH}_3\text{CN}$  vapour with the theoretical calculations. Experiment: +,  $298 \text{ K}$ ;  $\Delta$ ,  $298 \leq T \leq 350 \text{ K}$  (saturated vapour). Theory: ---, equation (6); -·-·-, equation (8).  $n(\chi/L = 0.2)$  has been calculated for  $T = 298 \text{ K}$ .

equations (6) and (8) it was assumed that the mean transport scattering cross section  $\langle\sigma_m(v)\rangle$  has a  $1/T$  temperature dependence in the temperature range under consideration /2, 13/.

It is seen that for  $n < 0.2/(\lambda\langle\sigma_m(v)\rangle)$  both quantum corrections may be effective but the experimental results are not sufficiently accurate to test the theory quantitatively.

However, the different behaviour of electrons in  $\text{NH}_3$  and  $\text{CH}_3\text{CN}$  is striking (compare fig.2 and fig. 3). In the case of  $\text{CH}_3\text{CN}$  the described density effects in the mobility - which are only of the first order with respect to  $n$  - seem to be precursors of a "sharper" mobility drop occurring at a further increase of the density of the dipole scatterers, possibly due to the appearance of localized electron states. To prove this idea it is necessary to extend Polischuk's theoretical calculations to higher densities.

It should be pointed out, however, that at the highest density of our investigation on electrons in  $\text{CH}_3\text{CN}$  (saturated vapour:  $n = 7.17 \times 10^{19} \text{ cm}^{-3}$ ,  $T = 398 \text{ K}$ ) the electron mobility is  $0.33 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . The mobility of anions (possibly  $\text{CH}_3\text{CN}_{\text{sol}}^-$ ) at this density is about  $0.16 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . This means that the electrons approach a behaviour which is reminiscent of heavy ions: therefore, electrons should be quasi-localized.

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#### References

- /1/ Krebs, P., Giraud, V., and Wantschik, M., Phys. Rev. Lett. **44** (1980) 211
- /2/ Krebs, P., J. Phys. Chem. **88** (1984) 3702
- /3/ Giraud, V. and Krebs, P., Chem. Phys. Lett. **86** (1982) 85
- /4/ Krebs, P. and Heintze, M., J. Chem. Phys. **76** (1982) 5484
- /5/ Mott, N.F. and Davis, E.A., "Electronic Processes in Non-Crystalline Materials" (Clarendon, Oxford 1979)
- /6/ Polischuk, A.Ya., Phys. Lett. **110** A (1985) 103  
Polischuk, A.Ya., J. Phys. B: At. Mol. Phys. **18** (1985) 829
- /7/ Polischuk, A.Ya., Teplofizika Vysokikh Temperatur **23** (1985) 10 (Translation)
- /8/ Krebs, P. and Lamatsch, B., J. Phys. B: At. Mol. Phys. **20** (1987) 4673
- /9/ Krebs, P. and Wantschik, M., J. Phys. Chem. **84** (1980) 1155
- /10/ e.g. Stockdale, J.A., Davis, F.J., Compton, R.N., and Klots, C.E., J. Chem. Phys. **60** (1974) 4279.
- /11/ Allis, W. P., Handb. Phys. **21** (1956) 413
- /12/ Altshuler, S., Phys. Rev. **107** (1957) 114
- /13/ Krebs, P., to be published
- /14/ Christophorou, L.G., Carter, J.G., and Maxey, D.V., J. Chem. Phys. **76** (1982) 2653
- /15/ Christophorou, L.G. and Christodoulides, A.A., J. Phys. B: At. Mol. Phys. **2** (1969) 71.