PHYSICAL REVIEW E **69**, 046401 (2004)

Negative ion formation and motion in a mixture of CCl_4 and Ar

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(Received 13 November 2003; published 14 April 2004)

This paper deals with the measurement of the mobility of negative ions in the mixtures of CCl_4 with Ar with the CCl_4 ratio up to 33.3%. The pulsed Townsend technique was employed to produce an integrated ionic avalanche over a range of the density-reduced electric field E/N for which ionization is either negligible or absent, and attachment processes are dominant, leading to the formation of mostly CCl_4^-. The E/N range of measurement was 1–50 Td ($1\ \text{Td}=10^{-17}\ \text{V cm}^2$). Our measurements strongly suggest that attachment is the dominant process and only negative ions are formed.

DOI: 10.1103/PhysRevE.69.046401 PACS number(s): 51.50.+v, 52.80.Dy, 52.20.−j, 52.25.Fi

I. INTRODUCTION

Carbon tetrachloride, CCl_4, is a volatile compound with several important technological applications, being used as an etching agent in microelectronics [1] as well as its importance in radiation chemistry and physics [2], the development of gaseous insulators and switching devices [3], the interpretation of electron swarm experiment [4], environmental concerns, and kinetic processes [5–7]. Although the CCl_4 molecule pollutes atmosphere harmfully and has been related to the so-called greenhouse effect [8] with global warming potential of 1800 and atmospheric lifetime of 35 years, yet that is low compared to gases such as SF_6 which is of global warming potential of 22 200 and atmospheric lifetime of 3200 years. Hence its uses as an alternative for sulfur hexafluoride in high-voltage applications can be of importance. Its mixture with other gases also is of importance not only for etching but also for finding (CCl_4) mixtures with other gases that would retain its thermal and insulating characteristics, while being substantially less harmful to the environment. The pulsed Townsend method is employed here since it is expected to have only one negative ion (CCl_4), hence eliminating the need for more complicated methods.

In this work we report the measurement of the mobility of the negative CCl_4 ions in Ar. The motivations were to determine to what extent one can present the measured mobility to one particular negative ion by operating at low enough E/N values in order to discard other processes that might obscure such identification. The mixture of Ar-CCl_4 is considered so that the collision processes to be considered are elastic electron-inert gas, electron-CCl_4 collisions, and possibly vibrationally inelastic electron-CCl_4 collisions, as well as electron attachment to CCl_4.

The Ar was chosen as an example of a gas with a momentum transfer cross section characterized by a Ramsauer-Townsend minimum. The theoretical integral cross section for e-CCl_4 scattering [9] shows a sharp decline below 2.0 eV. Extrapolating the theoretical data down to 100 meV collision energy results in a cross section as low as $1\times10^{-16}\ \text{cm}^2$. The estimated inelastic cross section for the e-CCl_4 [10] at 7.5 eV is about $2\times10^{-15}\ \text{cm}^2$, descending rapidly to about $5\times10^{-16}\ \text{cm}^2$ at 6.0 eV collisional energy. An estimate of $10^{-18}\ \text{cm}^2$ can be obtained from the extrapolation of this cross section to energies below 1.0 eV.

The electron attachment cross section at low electron energies to CCl_4 were reported by Hayashi [11] to be about $3\times10^{-14}\ \text{cm}^2$ at 25 meV electron energy and $2\times10^{-16}\ \text{cm}^2$ at 500 meV electron energy. These cross sections are in good agreement with those obtained using the power law approximation given by $\sigma(E)=0.5178E^{-1.88}$ resulting in the formation of CCl_4^-. The attachment cross section of Hayashi [11] agrees very well with those reported by Ken-ichi Kowari *et al.* [12]. The rate constant for the attachment of electrons to CCl_4 Refs. [11] and [12] show relatively large cross section leading us to conclude that the negative ions are rather dominant.

The negative ion signal observed in this work can only be identified with the CCl_4^- since the density-reduced electric field intensity E/N used here is kept small in order to have low electron energies. This would imply that ionization processes can be ignored.

II. EXPERIMENTAL APPARATUS

A pulsed Townsend apparatus recently built in this laboratory was used in the present measurements and it was described earlier in detail [13], brief description is provided in this section.

The Townsend chamber , shown in Fig. 1, consists of two parallel highly polished electrodes of 7 cm in diameter, with rounded edges. The upper electrode (anode) was composed of nonmagnetic stainless steel with a central hole of 1.5 cm covered with a flat mesh of high transmission (3 lines per mm) in order to permit the passage of a 10 ns duration, 355 nm wavelength, ultraviolet light beam of variable intensity. Once the UV light strikes the aluminum cathode, high photoelectron yield is produced. A micrometer mechanism was used in order to vary the two electrodes separation. During

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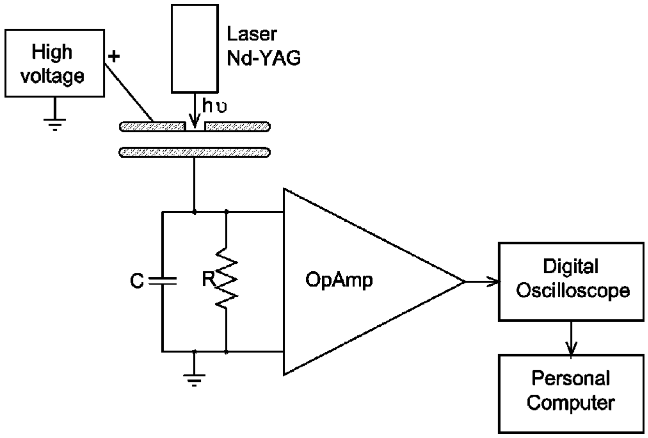

FIG. 1. Schematic diagram of the pulsed Townsend chamber apparatus.

this work, the separation of the two electrodes was kept constant at 13.6 mm and with an accuracy of 0.025 mm.

The high vacuum system consist of a 6 in., six way cross of nonmagnetic stainless steel that was evacuated down to about 1.2×10^{-6} Torr, using an $80\ \mathrm{l\,sec}^{-1}$ turbomolecular pump backed by a $1.5\ \mathrm{m}^3\mathrm{sec}^{-1}$ mechanical pump, before the injection of the gas. Gas pressure in the chamber was monitored by an absolute pressure transducer (MKS Baratron) with an accuracy of 0.03% at full range of 1000 Torr. Uncertainties in the gap voltage is estimated to be about 0.1%. All the measurements were performed at room temperature and within the range of 291–304 K and to an accuracy of 0.2%. The displacement current resulting from the charge carriers motion within the gap was detected by the insertion of an FET amplifier of 1 GΩ input impedance and 10 MHz bandwidth. In this case the current in the external circuit was integrated by the effective capacitor and resistance connected to the amplifier input. The third harmonic output of an INDI-YAG laser with a *Q*-Switch (10 ns FWHM) and maximum energy of 20 mJ was used. The Ar gas used in this work is of a high research grade of 99.999% purity. The CCl_4 vapor was prepared by introducing the liquid CCl_4 into a glass vessel that had two valves, one valve leading into a turbo pump, while the second leading to the vacuum chamber. The valve on the vacuum chamber side was kept closed, while that of the turbo pump side was opened. The air in the vessel was removed once the volume above the liquid CCl_4 was brought down to vacuum. When the boiling effect of the CCl_4 subsided, the turbo side valve was closed and the vacuum chamber side valve was opened to allow high purity CCl_4 vapor to be introduced into the discharge chamber. The electric field within the discharge gap was produced by high stability 0–5 kV regulated power supply with less than 10 mV ripple and was monitored by a calibrated 10 000:1 potential divider. The 355 nm laser beam was used to produce the initial photoelectrons. Space charge effects were avoided by keeping the cross section area of the laser beam large enough at about 70 mm^2. The photoelectrons were produced at the center of the electrode system where the electric field is homogeneous. Due to the slow transient time of the avalanches (maximum of 5 ms), the estimated bandwidth is sufficiently adequate. A 20 MHz oscilloscope was used to register the amplified avalanches and later to be stored on a personal computer for the analyses. A fast photodiode detecting the same laser pulse, provided the synchronized triggering of the oscilloscope.

III. RESULTS AND DISCUSSION

The action of the UV light initiated the instantaneous release of photoelectrons from the cathode. The electric field between the electrodes causes the photoelectrons to move towards the anode. According to the gas mixture and E/N values, the photoelectrons may ionize and/or attach to the gas neutrals. Due to the high mobility of the electrons in comparison to the ions, the ions remain practically where they were formed during the electron transit. Eventually the ions move to their corresponding electrodes on a different time scale. This would result in two different contributions, the fast electronic component, and a second slow ionic component. In the case that no ionization is assumed, under high pressure conditions (maximum 50 Torr), the photoelectrons liberated are attached to the CCl_4 molecules within few mean free paths from the cathode surface. This would lead into the formation of negative ions. Assuming strong attachment, the negative ion current during the electron transit is

$$i_n(t)=\left(\frac{n_0q_0}{T_n}\right)(1-\exp(-\eta\nu_e t)), \tag{1}$$

where n_0 is the photoelectron number, q_0 is the ion charge, η is the electron attachment coefficient, ν_e is the electron drift velocity, d is the discharge gap spacing, and ν_n is the negative ion drift velocity. Hence under the conditions of strong attachment, the negative ion current can reach its maximum value well before the electron transient time T_e. Within the ionic drift region $T_e\leqslant t\leqslant T_n$, the negative ion current is

$$i_n(t)=\left(\frac{n_0q_0}{T_n}\right)(1-\exp[-\eta(d-\nu_n t)]). \tag{2}$$

In the present experimental work, the displacement current is integrated at the input of a very high impedance amplifier which relies on the charging of the estimated 30 pF overall stray capacitance (gap, wiring, and preamplifier input capacitance) connected between the input terminals.

However, with the high gas pressure, ηd is very large $(\geqslant 10)$, then Eq. (2) would approximate to

$$V_n\approx\left(\frac{n_0q_0}{CT_n}\right)t. \tag{3}$$

The negative ion avalanche produced by fast ion conversion, travels toward the anode without any changes, since ion diffusion is neglected. When the input resistance of the amplifier is very large (1 GΩ as in the present case), then the passive resistance-capacitance circuit connected to the amplifier terminals behaves as an integrator as stated above. Hence the voltage between the input terminals of the amplifier is

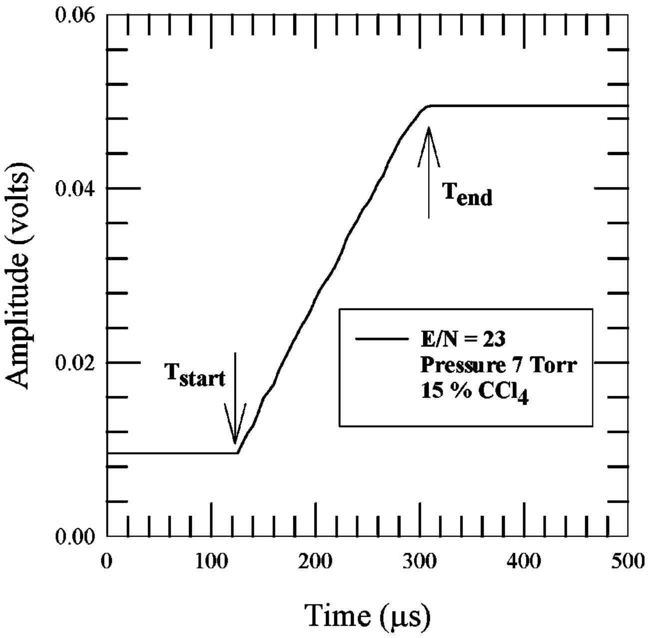

FIG. 2. Sample of negative ion transient from the 15% CCl_4 mixture.

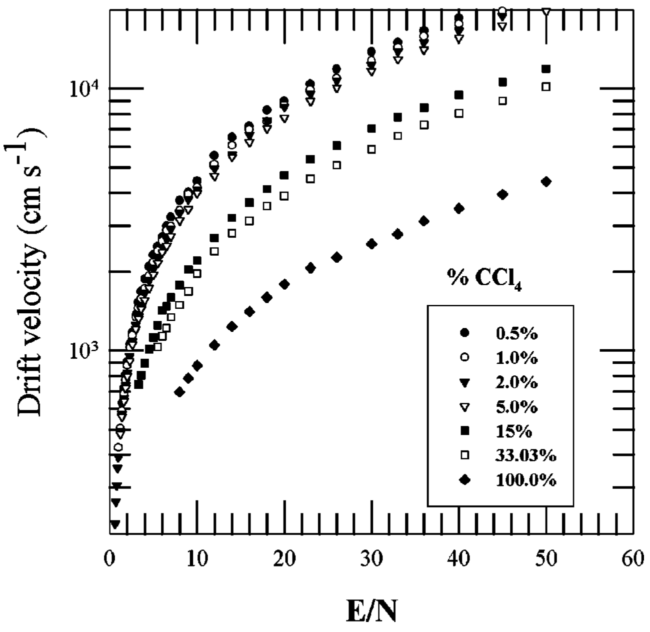

FIG. 3. The drift velocity of negative ions in CCl4-Ar mixtures, as a function of E/N for the following concentrations of CCl_4: 0.5, 1.0, 2.0, 5.0, 15.0, and 33.3 %. Also included the drift velocity of negative ions in CCl_4.

$$V_n(T_n)=\left(\frac{n_0q_0}{C}\right), \tag{4}$$

which represent a linear current growth to a maximum as shown in Fig. 2.

Figure 2 demonstrates the above mentioned behavior with the ion drift time given by $T_n=T_{end}-T_{start}$ and if there should be more than one negative ion species and most probably with different mobility, then the transient curve should show a break, which is absent from this curve. Therefore T_n and hence the drift velocities are determined.

The ν_n values are those for the average of at least three different pressures for the same E/N value and different gas mixture pressures. Therefore, the associated uncertainties would correspond to these averages. The maximum overall accuracy of the present measurements is estimated to be 4%. The drift velocity ν_n of the negative ions were obtained for CCl_4 concentration of 0.5, 1, 2, 5, 15, and 33.3 % with Ar and are presented in Fig. 3. Also included in Fig. 3 the drift velocity for CCl_4^- in 100% CCl_4.

Once the negative ions drift velocity were obtained for the above mentioned concentrations of CCl_4, the reduced mobility is calculated using the equation

$$K_0=(\nu_d/N_0)/(E/N), \tag{5}$$

where $N_0=2.69\times10^{19}$ cm^{-3} is the gas density at STP. Figure 4 shows the values of K_0 plotted as a function of E/N.

From Fig. 4, we can see that the mobility of the CCl_4^- increases with the decrease of CCl_4 concentration.

The mobility curves show that they remain constant over a fair range of their respective E/N ranges. This would imply that in such E/N values, the drift velocities are proportional to E/N and therefore the mobility remains constant as expected from Wannier's theory of ion motion in gases [14]. Due to this observation, it is possible to imply that the dominant ion-molecule interaction is due to the attractive part of the potential well in which the long range, attractive part of the interaction potential is dominant. The low E/N region as seen in Fig. 4, can be characterized by a linear dependance of the drift velocity as a function of E/N, or equally, a constant

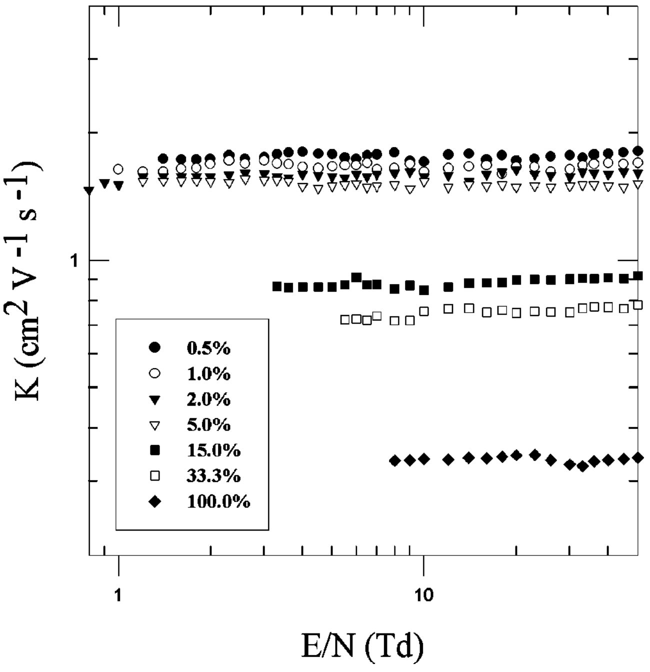

FIG. 4. The reduced mobility of negative ions (assumed CCl_4^-) in the CCl_4-Ar mixture. Also included the reduced mobility of CCl_4^- in CCl_4.

reduced mobility. In order to support the assumption that CCl_4^- is the predominant ion species in the mixture, a test of the low-field ($E/N \leqslant 10$ Td) ion mobility in the mixture with Blanc's law was conducted. The negative ion mobility in the nth gaseous component mixture [14,15] is given by

$$\frac{1}{K_{mix}} = \sum_{j=1}^{n} \frac{x_j}{K_{i,j}}, \tag{6}$$

where $K_{i,j}$ denotes the mobility of species i in the pure gas j, and x_j represents the molar fraction of gaseous species j in the mixture. To evaluate the mobility of the CCl_4^- in the mixture, the knowledge of the mobility of CCl_4^- in the pure gases CCl_4 and Ar is required. To our knowledge, there is no published data for such low-field mobility for the species involved in this work. Therefore to obtain such data, we measured the mobility of CCl_4^- in CCl_4 (100% CCl_4) as well as for small amount of CCl_4 (0.05%) in Ar. The low-field mobility for the above measurements were found to be 0.454 $cm^2\ V^{-1}S^{-1}$ for CCl_4^- in CCl_4 and 1.8 $cm^2\ V^{-1}\ S^{-1}$ for CCl_4^- in Ar. The calculated low-field mobility values are plotted in Fig. 5 as a function of CCl_4 percentage. It can be seen that the above calculated values are in good agreement with those measured in this work lending credit to the conclusion that the predominant ion species is that of CCl_4^-.

IV. CONCLUSION

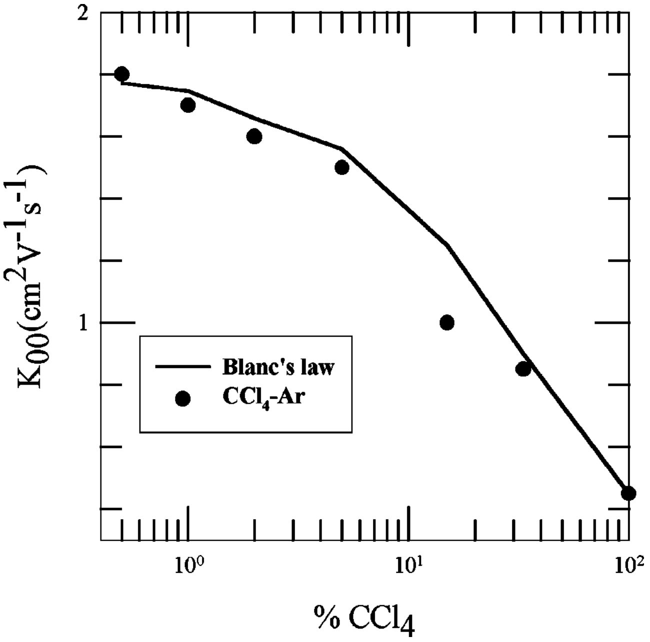

FIG. 5. Measured and calculated low-field mobility of CCl_4^- in Ar.

The time resolved pulsed Townsend technique allowed us to measure the CCl_4 negative ion mobility in the CCl_4-Ar mixture over a range of E/N values that extends up to 50 and gas pressure of 80 Torr. The characteristics of the measured transients, indicating that there is only one drifting ionic species. That, and the low E/N values used, led to the assumption that the majority ion species under investigation is CCl_4^-. This method proved to be highly sensitive for detecting negative ion signals even for small amounts of CCl_4 in the mixture. The relevance of electron attachment processes in these gas mixtures are desirable and it is our hope that the present data are of use for gas discharge simulation and complex ion chemistry of CCl_4-Ar mixtures.

ACKNOWLEDGMENTS

This research was supported by *PIFI*2 and PROMEP. The authors are grateful to Dr. J. de Urquijo for valuable input. We are grateful to A. Bustos and J. Rangel for their technical assistance.

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[1] R. A. Morgan, *Plasma Etching in Semiconductor Fabrication* (Elsevier, Amsterdam, 1985).
[2] A. Pagamenta, M. Kimura, M. Inokuti, and K. Kowari, J. Chem. Phys. **89**, 6220 (1988).
[3] L.G. Christophorou, Nucl. Instrum. Methods Phys. Res. A **268**, 424 (1988); L.G. Christophorouand and R.J. Van Brunt, IEEE Trans. Dielectr. Electr. Insul. **2**, 952 (1995).
[4] H. Itoh, Y. Miura, N. Ikuta, Y. Yakao, and H. Tagashira, J. Phys. D **21**, 922 (1988); K. Satoh, H. Itoh, Y. Yakao, and H. Tagashira, *ibid.* **21**, 931 (1988).
[5] L. G. Christophorouand S. Hunter, in *Electron-Molecule Interaction and their Applications*, edited by L. G. Christophorou (Academic, New York, 1984), Vol. 2, p. 317.
[6] L. G. Christophorou and S. Hunter, in Ref. [5].
[7] L. G. Christophorouand M. O. Pace, *Gaseous Dielectric IV* (Pergamon, New York, 1984).
[8] G.R. Burton, W.F Chan, G. Cooper, and C.E. Rion, Chem. Phys. **181**, 147 (1994).
[9] T. Marcio, N. Varella, P.P. Alexandra Natalensa, H.F. Betega Marcio, and A.P. Lima Marco, Phys. Rev. A **60**, 3684 (1999).
[10] L. David, H.F. Betega Marcio, G. Ferreira Luiz, and A.P. Lima Marco, J. Phys. B **33**, 5467 (2000).
[11] M. Hayashi, *Swarm Studies and Inelestic Electron Molecule collisions* (Springer, New York, 1987), p. 167.
[12] Ken-ichi Kowari, Ki Leung, and Bernie D. Shizgal, J. Chem. Phys. **108**, 1587 (1998).
[13] J. de Urquijo and F.B. Yousif, Phys. Rev. E **68**, 046406 (2003).
[14] E. W. MacDanial and E. A. Mason, *The Mobility and Diffusion of Ions in Gasses* (Wiley, New York, 1973).
[15] E. Mason and E. W. McDanial, *Transport Properties of Ions in Gases* (Wiley, New York, 1988).