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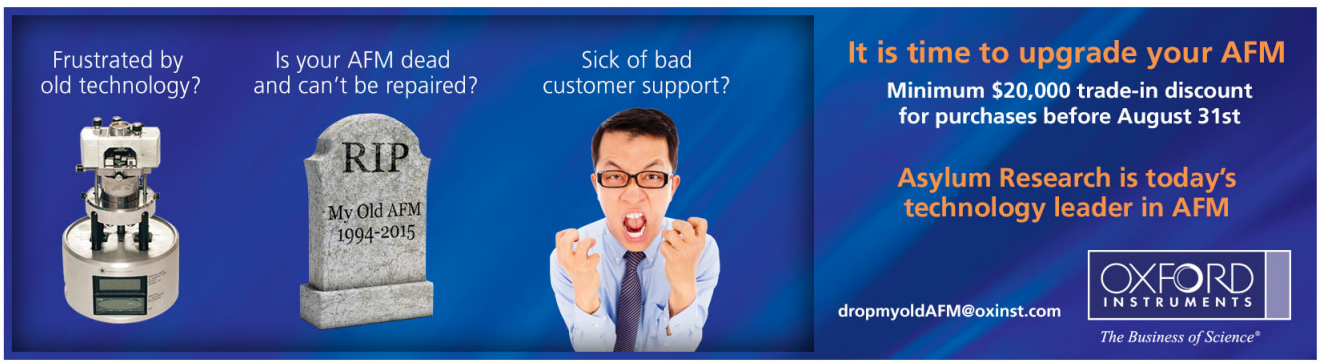

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Study of electron transport in hydrocarbon gases

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The drift velocity and the effective ionization coefficient of electrons in the organic gases, C_2H_2, C_2H_4, C_2H_6, CH_3OH, C_2H_5OH, C_6H_6, and $C_6H_5CH_3$, have been measured over relatively wide ranges of density-reduced electric fields (E/N) at room temperature (around 300 K). The drift velocity was measured, based on the arrival-time spectra of electrons by using a double-shutter drift tube over the E/N range from 300 to 2800 Td, and the effective ionization coefficient $(\alpha - \eta)$ was determined by the steady-state Townsend method from 150 to 3000 Td. Whenever possible, these parameters were compared with those available in the literature. It has been shown that the swarm parameters for these gases have specific tendencies, depending on their molecular configurations.
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I. INTRODUCTION

The elementary molecules containing carbon and hydrogen atoms (organic molecules) are of importance in manufacturing processes of graphene, carbon nanotubes (CNT),[1] carbon nanowalls (CNW),[2] diamond-like carbon (DLC) layers,[3] and so on. In such processes, the molecules in the gas phase are often made available in the formation and growth of these structures through intermediate plasma states. For the application of a variety of molecules, however, there still remain some data associated with electron collisions to be measured in order to supply fundamental parameters needed in designing with simulation models. Unfortunately, quantities such as electron swarm parameters have seldom been measured in some of these gases over the past few decades.

In this article, we present the experimental results on the electron transport parameters (swarm parameters) for the organic molecules, C_2H_2 (acetylene), C_2H_4 (ethylene), C_2H_6 (ethane), CH_3OH (methanol), C_2H_5OH (ethanol), C_6H_6 (benzene), and $C_6H_5CH_3$ (toluene), obtained from the arrival-time spectra (ATS) method using a double-shutter drift tube and a steady-state Townsend (SST) method. The experimental swarm parameters for these gases have been scarcely reported so far. Using the ATS method, we have measured the drift velocity, W_m (the mean arrival-time drift velocity) over the density-reduced electric field E/N from 300 to 2800 Td, while the effective ionization coefficient $\bar{\alpha}$ has been determined with the SST method for E/N values from 150 to 3000 Td. Here, $\bar{\alpha} = \alpha - \eta$, where α and η are the electron impact ionization and attachment coefficients, respectively. Although these parameters have been herein determined under simplified conditions (i.e., the drift velocity is deduced based on the spatial integration of an electron swarm while the effective ionization coefficient is measured under conditions of the steady-state equilibrium in the uniform electric field), these are the macroscopic quantities to describe the physical aspects accounting for the activity of electrons, particularly those involved ionizing reactions.

Through comparisons of the measured swarm coefficients among the gases, it is shown that these have specific tendencies, which depend on their molecular structures (e.g., normal chain or circularity types and the presence or absence of methyl or hydroxyl in the molecules). Some of the data have been measured for the first time, to our knowledge. It is important to remark that these basic characteristics of electron transport are very useful in a variety of discharge applications with these gases.

II. EXPERIMENTAL METHOD

A. Arrival-time spectra method

The measurement of the drift velocity was performed based on the ATS method[4] for evaluating the drift velocity W_m, which is defined from the ATS of electrons as

$$W_m = \frac{d\langle t \rangle}{dz}. \tag{1}$$

Here, $\langle t \rangle$ represents the average of the arrival-time of electrons at a position z in the drift tube. The experiment is conducted using a double-shutter drift tube, in which the arriving electrons are collected by the electrode (with shutter-2) at a certain distance from the cathode (with shutter-1) to release initial electrons.[4] The drift velocity, W_m, is deduced by dividing the mean time of arrival of electrons by the distance between the electrodes. The experimental apparatus and procedure for the ATS method were the same as those described by Hasegawa *et al.*[5] In the present study, the position of the collector plate was set at four locations, and the final value of drift velocity was determined by averaging the values determined at the four cases for each value of E/N.

B. Steady-state Townsend method

The effective ionization coefficient $\bar{\alpha}$ is given by

$$\bar{\alpha} = \frac{1}{N(z)} \frac{dN(z)}{dz} \tag{2}$$

$$\text{with} \quad N(z) = \int_0^\infty n(z,t)dt, \tag{3}$$

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where $n(z,t)$ is the electron number density at a position z and time t. Under the SST conditions, the electron current growth, I, is given by

$$I = I_0 \frac{\frac{\alpha}{\alpha-\eta}\exp\{(\alpha-\eta)d\} - \frac{\eta}{\alpha-\eta}}{1-\gamma_T\frac{\alpha}{\alpha-\eta}[\exp\{(\alpha-\eta)d\}-1]}, \quad (4)$$

where d is the gap spacing between the electrodes, I_0 is the initial current value, and γ_T is the secondary coefficient, respectively. To obtain the effective ionization coefficient, we used the SST method since it provides a more precise value of this coefficient than that obtained by the ATS method.

In the experiment for the organic gases in this study, electron attachment is significant, while the secondary coefficient γ_T was found to be negligible. Thus, Eq. (4) readily reduces to

$$I = I_0\left[\frac{\alpha}{\alpha-\eta}\exp\{(\alpha-\eta)d\} - \frac{\eta}{\alpha-\eta}\right]. \quad (5)$$

We determined α and η by fitting this equation to the relation between the current and the gap length using a linearized least-squares method.

The experimental apparatus and analytical procedures for the SST method are basically same as those given by Hasegawa *et al.*[6,7] The current measurement was repeated 12–26 times for each gap length and E/N, and the effective ionization coefficient was determined by averaging the values from the corresponding current measurements.

C. Purity of the gases and experimental conditions

The purity of the gases used and the experimental conditions for the field strength and gas pressure are listed in Table I. The drift length between the cathode and shutter-2 to collect electrons in the ATS experiment was 10–40 mm, and the gap length of the electrodes in the SST experiment (using the Harrison type electrodes) was 2–15 mm. Both experiments were performed at room temperature (295–300 K), except for C_6H_6 and $C_6H_5CH_3$, which were performed at about 60 °C.

III. RESULTS AND DISCUSSION

Figure 1 shows a comparison of the drift velocities W_m obtained for all gases. Two general tendencies are apparent:

TABLE I. Experimental conditions in this study.

Gas	Purity (%)	Reduced electric field, E/N (Td)		Pressure (Torr)	
		ATS	SST	ATS	SST
C_2H_2	99.99	300–2500	140–3000	0.1–0.8	0.2–17
C_2H_4	99.999	300–2500	140–3000	0.1–0.7	0.2–17
C_2H_6	99.95	300–2500	130–3000	0.1–0.7	0.2–8.0
CH_3OH	99.8	300–2300	150–3000	0.1–0.8	0.4–9.0
C_2H_5OH	99.5	300–2500	100–3000	0.1–0.8	0.4–11
C_6H_6	99.7	300–2800	100–3000	0.1–0.6	0.2–22
$C_6H_5CH_3$	99.7	300–2300	100–3000	0.1–0.6	0.2–22

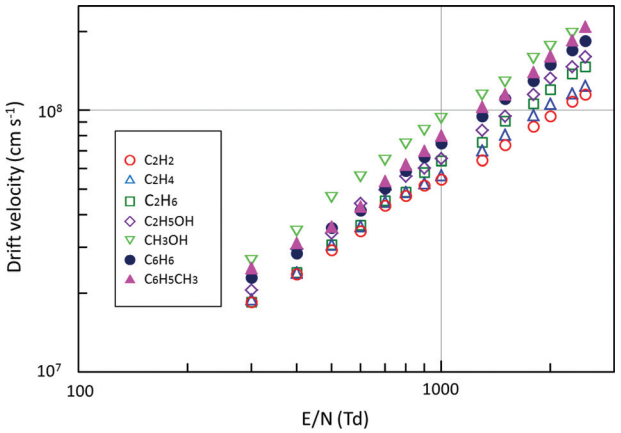

FIG. 1. Comparison of the drift velocity (the mean arrival-time drift velocity, W_m).

the value of W_m is smaller as the molecular weight of the gas molecules becomes smaller for the normal chain structure cases of C_2H_2, C_2H_4, and C_2H_6, while W_m is larger for the gas molecules containing the hydroxyl radical (-OH) than for those without it. Figure 2 shows the drift velocities for C_2H_2, C_2H_4, and C_2H_6 in comparison with the data found in the literatures.[8–12] Our present results are in good agreement with those from other investigations from 300 to 1000 Td. To the best of our knowledge, the drift velocities in these gases for E/N above 1000 Td have been measured for the first time in this study.

The density-normalized effective ionization coefficient for all gases under study is shown in Fig. 3. In general, the ionization coefficient for the cyclic molecules, C_6H_6 and $C_6H_5CH_3$, is smaller than that for the others, particularly in the low E/N region below 500 Td. The results are separately shown in Figs. 4–6 for three groups: Fig. 4 for C_2H_2, C_2H_4, and C_2H_6, Fig. 5 for CH_3OH and C_2H_5OH, and Fig. 6 for C_6H_6 and $C_6H_5CH_3$, and compared with other previously reported data.[13–16] As in Fig. 4, although there exists a slight difference between our results and other investigations for each gas, the ionization coefficient in C_2H_6 is larger than those for the other two molecules over the E/N range in this study. As regards CH_3OH, our result is in good agreement

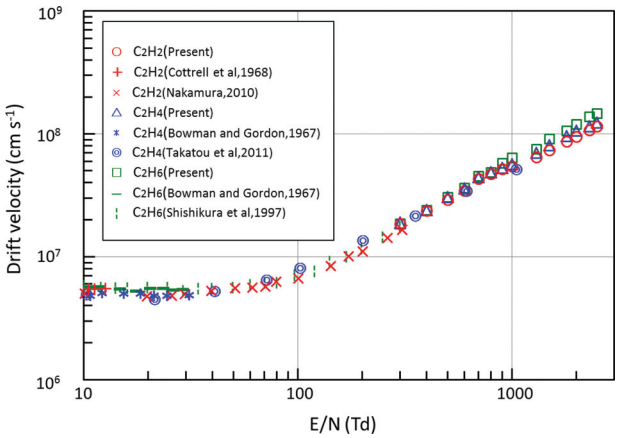

FIG. 2. Drift velocities for C_2H_2, C_2H_4, and C_2H_6, in comparison with the data from other investigations. Here, the present data are for the mean arrival-time drift velocity (W_m).

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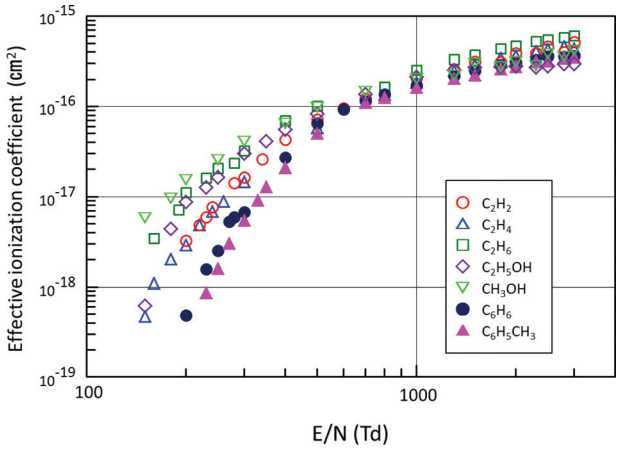

FIG. 3. Comparison of the effective ionization coefficient ($\bar{\alpha}/N = (\alpha - \eta)/N$).

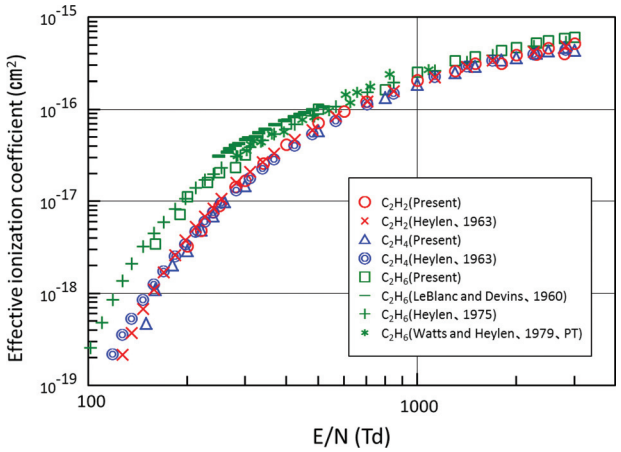

FIG. 4. Effective ionization coefficients ($\bar{\alpha}/N = (\alpha - \eta)/N$) for C_2H_2, C_2H_4, and C_2H_6, in comparison with the data from other investigations.

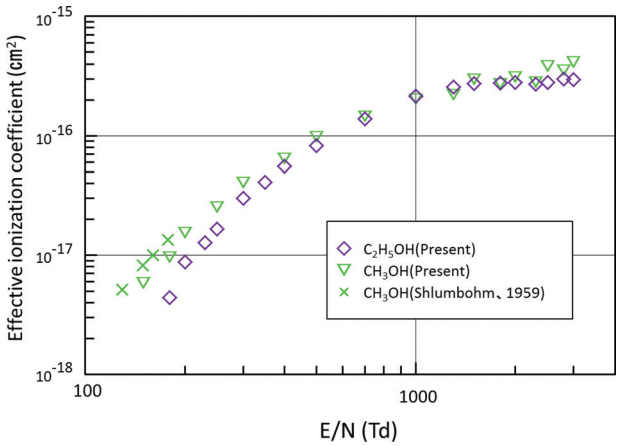

FIG. 5. Effective ionization coefficients ($\bar{\alpha}/N = (\alpha - \eta)/N$) for CH_3OH and C_2H_5OH in comparison with the data by Shlumbohm (1959).

with that of Ref. 17 below E/N = 200 Td (see Fig. 5). However, the ionization coefficient for C_6H_6 is up to a factor of 2 larger than that of Ref. 18 for E/N from 400 to 800 Td as shown in Fig. 6. The ionization coefficients for C_2H_2 and

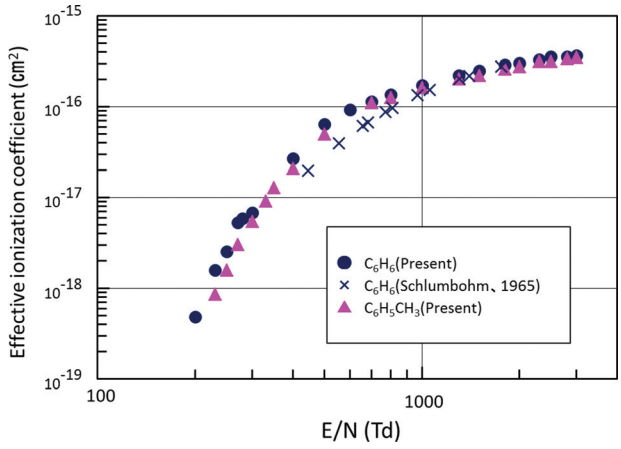

FIG. 6. Effective ionization coefficients ($\bar{\alpha}/N = (\alpha - \eta)/N$) for C_6H_6 in comparison with the data by Shlumbohm (1965) and for $C_6H_5CH_3$.

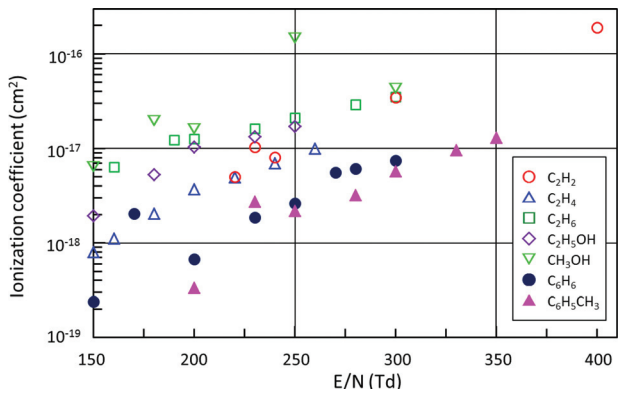

FIG. 7. Comparison of the ionization coefficient (α/N) for the E/N range from 150 to 400 Td.

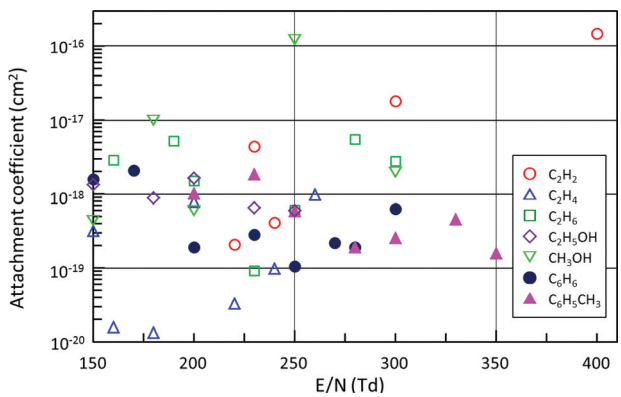

FIG. 8. Comparison of the electron attachment coefficient (η/N) for the E/N range from 150 to 400 Td.

C_2H_4 for E/N above 2000 Td, CH_3OH and C_2H_5OH for E/N above 200 Td, and C_6H_6 for E/N above 2000 Td have not been reported previously, and the coefficients in $C_6H_5CH_3$ for E/N from 200 to 3000 Td have been measured for the first time. In Figs. 7 and 8, the ionization coefficient (α/N) and the electron attachment coefficient (η/N) are plotted separately over a relatively low range of E/N (150–400 Td). As shown in Fig. 8, the resultant values for the attachment

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TABLE II. Ratio of the standard deviation to the mean value.

	ATS				SST					
	σ/m (max.)		σ/m (min.)		Number of positions	σ/m (max.)		σ/m (min.)		Number of current measurements
Gas	σ/m (%)	E/N (Td)	σ/m (%)	E/N (Td)	N	σ/m [%]	E/N (Td)	σ/m (%)	E/N (Td)	n
C_2H_2	4.01	2500	0.349	500	4	9.97	800	1.36	2800	12–23
C_2H_4	3.90	2500	0.225	1300	4	7.80	500	0.57	800	13–23
C_2H_6	3.71	1800	0.182	1500	4	9.51	230	3.23	1000	13–23
CH_3OH	5.27	1000	0.290	700	4	8.90	180	0.54	200	14–26
C_2H_5OH	4.79	2500	0.395	900	4	9.85	200	0.77	500	14–23
C_6H_6	5.51	2300	0.192	2500	4	5.53	2000	1.57	700	13–23
C_6H_5CH3	4.16	1500	0.300	700	4	6.01	700	0.92	2500	12–19

coefficient scatter widely, presumably due to the presence of impurities and for also a statistical reason, and are generally much smaller than the corresponding ionization coefficients over this range of E/N.

The uncertainty of the values obtained for these coefficients was evaluated by the ratio of σ/m (σ: the square of unbiased variance and m: the average) for the cases of drift distances in the ATS observations and for the iteration of current measurements in the SST method. The maximum and minimum values of σ/m are shown in Table II, where m and σ are defined by

$$m = \frac{1}{n}\sum_{i=1}^{n} x_i \tag{6}$$

and

$$\sigma = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(x_i - m)^2}. \tag{7}$$

Here, x_i represents a measured value and n is the number of values.

The reason why the ionization coefficients in the ring type molecules (C_6H_6 and $C_6H_5CH_3$) are smaller than those of the chain type molecules as in Fig. 3 may be attributable to the energy transfer from the incident electron to a "π-electron," absorbing collision energy into the circular configuration,[19] which in turn decreases the ionization probability of the molecule. With regard to the presence of radical -OH in the molecules, we can see a major difference between C_2H_5OH and C_2H_6 in Fig. 3, where the ionization coefficient for C_2H_5OH is much smaller than that for C_2H_6 for E/N above 1800 Td. This may indicate that -OH acts as a less significant factor than -H for the ionization process over this E/N region by an electron-attracting effect in the molecule. As a matter of fact, the ionization probability and the behavior of electron swarms should be discussed based on the electron collision cross sections. Unfortunately, to our knowledge, the cross section data for C_6H_6 and $C_6H_5CH_3$ and for CH_3OH and C_2H_5OH are insufficient to explain electron transport parameters in terms of them. However, one feature in Fig. 4 can be interpreted from a view point of the electron collision cross sections, namely, the initial rise of the ionization cross section for C_2H_6 at the energy just above the ionization threshold is the largest, while the momentum transfer cross section is the smallest among the three molecules.[10,12,20]

Although the swarm parameters sometimes differ depending on their definitions, particularly at the high E/N region in which the ionization process can occur (e.g., Ref. 4), the exact definition of some parameters and their measurement methods have been established.[21] Our study presents experimental parameters for the mean arrival-time drift velocity (W_m) and the Townsend effective ionization coefficient ($\bar{\alpha}$) (including the separate result for the ionization coefficient α and the attachment coefficient η over a low range of E/N). The resultant data for the swarm parameters in the organic gases treated here can be used to predict quantitative properties of electron transport in the gases under the action of electric fields.

IV. CONCLUSION

In this study, the drift velocity (W_m) of electrons and the effective ionization coefficient ($\alpha - \eta$) were measured in the organic gases (C_2H_2, C_2H_4, C_2H_6, CH_3OH, C_2H_5OH, C_6H_6, and $C_6H_5CH_3$) for relatively wide ranges of E/N. The drift velocity was obtained by using a double-shutter drift tube and the effective ionization coefficient was determined by the SST method. Some of them were measured for the first time. We recognize that these parameters have specific tendencies, depending on the molecular structure of the gases, such as chain-like or ring-type, and also by the presence or absence of -OH in the molecule. Some of the results were compared with those in the literature, and good agreement was observed in general. The results in this study on the swarm parameters would be beneficial in a variety of applications of these gases in weakly ionized plasma states.

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