# A New Method for Measuring the Diffusion Coefficient in a Gas Phase

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A new and fast method for measuring the diffusion coefficients of binary gas mixtures using ion mobility spectrometry (IMS) has been developed. In this method, the sample is injected as a short pulse into the flowing drift gas, forming a Gaussian concentration profile inside the drift region. This Gaussian cloud is irradiated with a fast moving swarm of electrons to create negative ions. The flash of electrons is so short that the negative ions do not move much during the exposure time. The ions then drift toward the detector, where they are collected. The collected ion signal pattern reflects the spatial distribution of the sample inside the cloud at the time of exposure. This is repeated in intervals of 300−400 ms to monitor the spatial spreading of the molecules in the drift region. Consecutive IMS spectra show the evolution of the cloud over time. The collected spectra are fit to Gaussian functions to extract diffusion coefficients. Using this method, the diffusion coefficient of $O_2$, $CHCl_3$, and $C_2H_2Cl_2$ were measured, and the results are in good agreement with the previously reported experimental data.

## I. Introduction

The diffusion coefficient is an important molecular characteristic that can yield information concerning molecular size. It provides a more direct means of investigating intermolecular potential than other transport properties, because it is determined primarily by collisions between unlike molecules. There are many techniques that can be applied to measure diffusion coefficients. Marrero,[1] Cussler,[2] and Jost[3] reviewed most experimental methods for measuring diffusion coefficients, such as two-bulb apparatus, evaporation tube, capillary leak, steady-state evaporation, unsteady-state evaporation, sound absorption, light scattering, interferometric methods, and Taylor dispersion, as well as gas chromatography (GC) and nuclear magnetic resonance (NMR) methods.

All different experimental methods for measuring the diffusion coefficient can be classified as two general types. For the first, a steady flow of the sample in the second gas is prepared and the profile of the concentration in different coordinates is employed for the measurement. For the second general type of measurement, a concentrated sample diffuses and the unsteady concentration profile is detected over time or both over time and in spatial coordinates.

GC techniques that have been for measuring the diffusion coefficient, both in its original form as well as in various modified forms, have been reported by Huang et al.,[4] after their introduction by Giddings and Seager in 1960.[5] In GC broadening techniques, the decay of a gas pulse that had been injected into a GC column with a constant velocity of the carrier gas was used to measure the diffusion coefficient (see the review by Maynard and Grushka[6]). In GC stopped-flow techniques, the decay of a stop peak over time was used to determine the diffusion coefficient with much shorter columns than those used in broadening techniques.[7,8] Reversed-flow techniques, which have sharper peaks, have also been used to measure diffusion coefficients.[9] Although the latter methods are much faster than the former ones, the experiment is still time-consuming.

In 1964, Mueller and Cahill[10] used mass spectrometry to measure the diffusion coefficient of some binary gas mixtures. They used the method proposed by Ney[11] and applied by Winn[12] for measurement of the self-diffusion coefficient. In this method, the rate of change in concentration that occurs in the diffusion in two connected bulbs of different gases was measured using a mass spectrometer. In a different way, mass spectrometry has been used in the back-diffusion method[13,14] for analysis of the stationary exponential concentration of one gas in a tube, diffusing against a constant flow of another gas. Plumb and Ryan[15] have reported a mass spectrometric method to measure the diffusion coefficient of $O(^3P)$ atoms in helium. In this method, the arrival time distribution of O atom pulses is obtained using a mass spectrometer for different known lengths of flow tubes, and the standard deviation of the distribution is used to estimate the diffusion coefficient.

A variety of optical methods[16−20] has been used to determine the diffusion coefficient. For some optical methods, a change in the refractive index of the diffusive medium is used to determine the diffusion coefficient. Photonic crystal fibers have been used recently to determine the diffusion coefficient.[21] In this method, the gas concentration within the air-hole columns of a fiber was monitored by measuring the attenuation of light through the photonic crystal that is caused by the evanescent wave absorption of light by the gas sample.

In this article, we present a new method for monitoring the diffusion process and measuring the diffusion coefficient using ion mobility spectrometry (IMS) in negative-ion mode. The diffusion coefficient of test compounds (oxygen, chloroform, and dichloroethane) were measured by this method and compared with the values obtained from other methods.

## II. Methodology

The new method is basically a pulse decay method in which a short pulse of the molecular sample in gas phase is injected to the nitrogen flowing gas and then the decay of that pulse is

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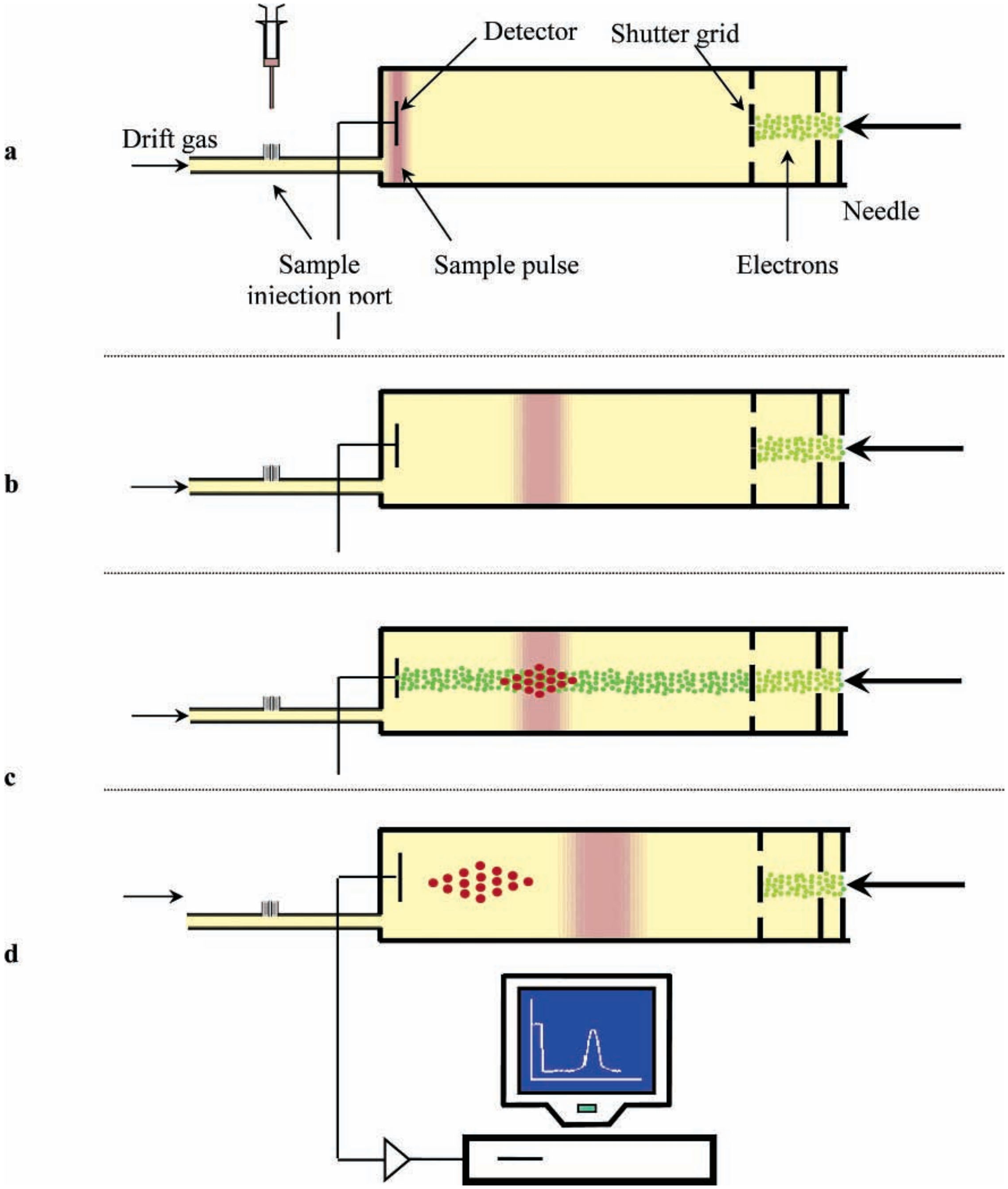

**Figure 1.** Schematic diagram of the method for measuring the diffusion coefficient: (a) the sample was injected to the drift gas; (b) the sample pulse is shifted to the drift region by the flowing drift gas; (c) electrons are released from the shutter grid for 50 $\mu$s, and electrons are captured by the sample molecules to form negative ions (the spatial distribution of the product ions reflects the distribution of the molecular pulse); and (d) ions drift toward the detector, and the ion signal pattern reflects the spatial distribution of the sample at the time of exposure. This process is repeated in fraction-of-a-second intervals so that each time, the next bunch of electrons experiences a wider molecular pulse.

monitored. In this method, an ion mobility spectrometer in negative ion mode was used. The IMS instrument was equipped with an intense electron source, as described previously.[22] The sample is injected as a short pulse into the flowing drift gas to form a Gaussian cloud inside the drift region. The molecular cloud expands as it moves in the drift gas and spreads over a wider area in the tube. At the same time, the cloud is irradiated with a fast moving swarm of electrons, which are released from the shutter grid, to create negative ions via an electron attachment reaction. These ions created movement in the drift region toward the detector. The ion signal pattern reflects the spatial distribution of the sample inside the cloud at the exposure time. The exposure time is very short, with respect to the drift time of the ions, so that their displacement is not significant. This procedure is repeated several times in certain intervals. The procedure is schematically illustrated in Figure 1. For each subsequent electron pulse, the ion signal is expected to spread and shift over time, when compared to the previous ion signal. This result arises from the fact that the time interval between pulses is sufficient to observe a change in the molecular cloud concentration profile due to the diffusion. The consecutive IMS spectra show the evolution of the cloud over time, in a manner similar to a movie. Figure 2 shows the expected spectra that are due to movement and diffusion of the sample inside the drift region. A simple one-dimensional model is used to measure the diffusion coefficient. It will be shown that the change in

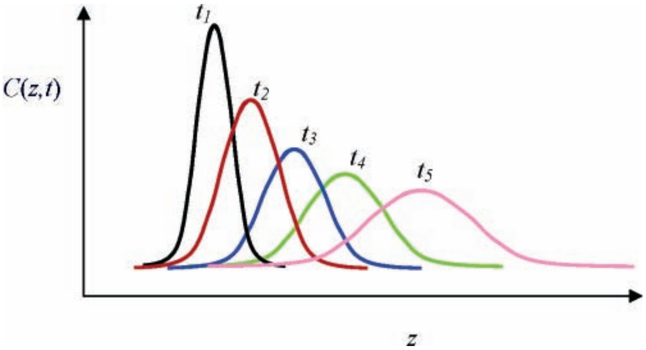

**Figure 2.** Diffusion of an infinite sharp pulse in a flowing gas is a Gaussian profile that decays and shifts.

the standard deviation of the Gaussian distribution against the time can be used to determine the diffusion coefficient.

## III. Experimental Section

The ion mobility spectrometer used in this study was constructed in our laboratory at the Isfahan University of Technology. The instrument was similar to that described previously.[22] In summary, the IMS cell was a glass tube, with an inner diameter (ID) of 4 cm and a length of 19 cm, on which 15 stainless-steel guard rings were mounted. The cell was equipped with an electron source, based on a negative corona discharge in pure nitrogen. A curtain gas (pure nitrogen) was used to prevent the diffusion of sample into the discharge. The drift region was 11 cm and a voltage of 4000 V was applied to create the drift field. The shutter grid opening time was 50 $\mu$s in intervals of 340 ms. The data were collected only for 20 ms after the shutter grid opening time, because it was long enough to record all ions. The ion signal was fed into a computer via an analog/digital (A/D) converter after amplification.

The drift gas supply used in this project was pure nitrogen (99.999% purity). Water vapor and other contamination were removed by passing the gas through a 13X molecular sieve (Fluka) trap before entering the ion mobility spectrometer. The flow of the curtain and the drift gas was typically 100 and 200 mL/min, respectively. The drift gas inlet was behind the collector plate, at a distance of 1.5 cm from that component. This helped avoid turbulence in the drift tube in front of the collector. The collector plate had many holes, to allow the gas pass through it smoothly. All chemical compounds used in this study, except $O_2$, were purchased from Fluka and were used without further purification. Headspace vapor of the test compounds were used for the sample gas. The experiment was performed at ambient pressure (630 Torr) and the specified temperature, as shown in Table 1.

In this experiment, the sample was directly injected into the drift flow, so that it entered the drift tube from the detector side. The injection was carried out manually using a glass syringe and was performed as quickly as possible, to create a narrow pulse of sample. Before injection, the sample was consecutively diluted to reach an appropriate concentration, so that few electrons were consumed. This was essential to simplify the model. Further explanation is given in the Results and Discussion section.

## IV. Theory

Because the decay of the molecular pulse in the flowing gas is monitored, it is essential to know the final shape of the pulse and its evolution over time. In addition, because the observation is conducted by detecting the ions that are formed within that molecular pulse, it is necessary to determine the final distribution and shape of the ion cloud and its behavior over time.

**A. Distribution of the Sample.** In our experiment, the velocity of the flowing gas is low enough to ensure laminar flow inside the drift tube. In addition, the measurement is performed in a small portion (2 mm) in the center part of the tube (4 cm ID). Thus, the concentration of the sample in the vicinity of the symmetry axis ($z$) of the tube can be considered to be invariant, with respect to the $x$- and $y$-coordinates. Consequently, it may be reduced to a simple one-dimensional model, so that the mass-balance equation in a volume element on the symmetry axis can be written as

$$\frac{\partial C_z}{\partial t} = D_{12}\left(\frac{\partial^2 C_z}{\partial z^2}\right) - \frac{\partial(C_z\bar{v})}{\partial z} \tag{1}$$

where $C$ is the concentration, $z$ the coordinate, $t$ the time, $D_{12}$ the diffusion coefficient of sample 1 in gas 2, and $\bar{v}$ the average velocity of the flowing gas. In this equation, the two terms are attributed to the diffusion and the convection, respectively. If the initial pulse of the sample is assumed to be a delta function at $t = 0$,

$$C(z,t = 0) = \frac{M}{A}\,\delta(z) \tag{2}$$

such that

$$\delta(z) = \begin{cases} \dfrac{1}{\epsilon} & (\text{for } z = 0) \\ 0 & (\text{for } z \neq 0) \end{cases}$$

where $M$ is the total amount of the sample in the system and $A$ is the cross- sectional area over which the diffusion is occurring. If the drift gas is not flowing, then the concentration profile over the $z$-coordinate at time $t$ is expected to be a Gaussian function:[2]

$$C(z,t) = \frac{M/A}{\sqrt{4\pi D_{12}t}}\exp\left(-\frac{z^2}{4D_{12}t}\right) \tag{3}$$

**TABLE 1: Diffusion Coefficients Measured in This Work, in Comparison with Values Obtained from Another Method (Given in Ref 6)[a]**

| | IMS Method | | | | GC Method (ref 6) | |
|---|---|---|---|---|---|---|
| | At 630 Torr and the Specified Temperature | | Corrected to 760 Torr and the Specified Temperature | | At 760 Torr and the Specified Temperature | |
| compound | $T$ (°C) | $D$ (cm$^2$/s) | $T$ (°C) | $D$ (cm$^2$/s) | $T$ (°C) | $D$ (cm$^2$/s) |
| $O_2$ | 33 | $0.25 \pm 0.01$ | 25 | $0.25 \pm 0.01$ | 25 | 0.23 |
| $CHCl_3$ | 60 | $0.14 \pm 0.02$ | 85 | $0.14 \pm 0.02$ | 85 | 0.135 |
| $C_2Cl_4$ | 32 | $0.12 \pm 0.01$ | 32 | $0.12 \pm 0.01$ | | |

[a] To compare the results under similar conditions, our results were converted to suitable pressures and temperatures using eq 15.

Although the equation was derived for the ideal case (i.e., when the neutral gas sample pulse is assumed to be so narrow in time that can be treated as a delta function), it is still valid to describe the evolution of any Gaussian peak from time $t_1$ to $t_2$, regardless of how that Gaussian peak has been formed.

This equation is applicable when there is no convection. However, if the drift gas is flowing with a linear velocity of $\bar{v}$; this is equivalent to a situation where the $z$-axis is shifting over time by $\bar{v}t$. Therefore, the distribution will be given as

$$C(z,t) = \frac{M/A}{\sqrt{4\pi D_{12}t}} \exp\left[-\frac{(z-\bar{v}t)^2}{4D_{12}t}\right] \tag{4}$$

The spatial concentration profile is a Gaussian function, distributed around $z = \bar{v}t$, which shifts linearly and decays exponentially over time (see Figure 2). Here, for the sake of simplicity, the laminar broadening has been neglected. The error is not expected to be considerable, because the linear speed of the gas in the drift region is low.

Equation 4 explains the spatial and time dependency of the concentration of the neutral sample molecules. Nevertheless, in the real experiment, only the ions can be monitored, not the neutrals. Hence, it is necessary to know the actual distribution of the ions resulting from such a distribution of neutrals.

**B. Distribution of Ions.** Negative ions are produced via an electron attachment reaction, such as

$$M + e \xrightarrow{k} M^- \tag{5}$$

The production rate of $M^-$ is

$$-\frac{d[e]}{dt} = \frac{d[M^-]}{dt} = k[M][e] \tag{6}$$

in which [M], $[M^-]$, and $[e]$ are the concentration of the sample molecules, the ions, and the electrons, respectively. For a short period of the exposure time, $\Delta t$, the concentration of the ions produced at a particular point, $[M^-]_z$, will be

$$[M^-]_z = k[M]_z[e]_z\Delta t \tag{7}$$

where $[M]_z$ and $[e]_z$ are the concentration of the neutral molecule and the electrons at point $z$. $[M]_z$ (i.e., the concentration of M, as a function of $z$) is identical to $C(z,t)$, which is known from eq 4. Thus,

$$[M^-]_z = k\frac{M/A}{\sqrt{4\pi D_{12}t}}[e]_z\Delta t \exp\left(-\frac{(z-\bar{v}t)^2}{4D_{12}t}\right) \tag{8}$$

In this equation, the concentration of electrons at each point, $[e]_z$, is not known. As the electron pulse moves through the sample cloud, its concentration decreases, because of the electron capture process. If it goes through a uniform concentration of sample, it decays exponentially; however, in this case, it goes through a Gaussian sample distribution. Therefore, its decay is no longer a simple exponential decay. This situation is depicted in Figure 3. Equation 6 shows that one can drive the remaining electrons at a particular point $z$ as

$$\int_{[e]_0}^{[e]_t} \frac{d[e]}{[e]} = -\int_0^t k[M]_t\, dt \tag{9}$$

Here, $[M]_t$ is a function of $t$, because, as the electron swarm goes through the sample cloud, the concentration of M changes. If the electrons move with an average velocity of $w$ (where $w = -dz/dt$), then $[M]_t$ and $dt$ may be substituted with $[M]_z$ and $dz/w$, respectively, to give

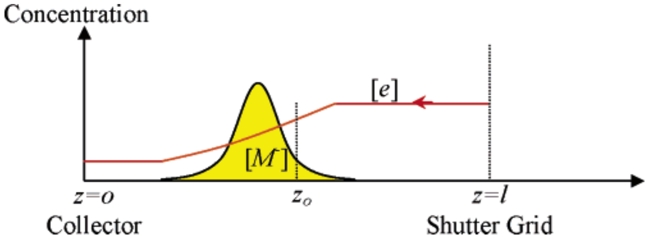

**Figure 3.** Changes in electron concentration when passing through a cloud of electrons attached to the sample in the drift tube.

$$[e]_z = [e]_0 \exp\left(\frac{k}{w}\int_l^z [M]_z\, dz\right) \tag{10}$$

Combining eqs 4, 7, and 10 gives the final distribution of the negative ions, as a function of time and spatial coordinates:

$$[M^-]_z = k\frac{M/A}{\sqrt{4\pi D_{12}t}}\Delta t \exp\left(-\frac{(z-z_0)^2}{4D_{12}t}\right)[e]_0 \times \exp\left(\frac{k}{w}\int_l^z \left(\frac{M/A}{\sqrt{4\pi D_{12}t}} \exp\left[\frac{z-z_0}{4D_{12}t}\right]^2\right) dz\right) \tag{11}$$

where $z_0 = \bar{v}t$. The integration of a Gaussian function is an error function,[23] and then the equation may be rewritten as

$$[M^-]_z = \frac{kM/A}{\sqrt{4\pi D_{12}t}}\Delta t[e]_0 \exp\left(-\frac{z-z_0}{4D_{12}t}\right) \times \exp\left[\frac{kM/A}{8wD_{12}t}(\mathrm{erf}(z) - \mathrm{erf}(l))\right] \tag{12}$$

in which erf($q$) is the error function of $q$, which is defined as

$$\mathrm{erf}(q) = \frac{2}{\sqrt{\pi}}\left(q - \frac{q^3}{3} + \frac{q^5}{10} - \frac{q^7}{42} + \frac{q^9}{216} - \cdots\right) \tag{13}$$

Equation 12 gives the profile of the ion distribution after passing a swarm of electrons through a Gaussian cloud. The error functions can be numerically calculated and the experimental data can be fit to an expression such as eq 12 to obtain the diffusion coefficient. However, if the concentration of sample is low enough so that the change in electron concentration is negligible after passing through the sample, eq 8 can simply be used instead of the complex expression in eq 12. In this case, the profile is very similar to a Gaussian shape, except for it being slightly distorted from being fully symmetric, because of the last term of eq 12.

## C. Results and Discussion

To evaluate the method, several test compounds, including oxygen, chloroform, and tetrachloroethylene, were selected. Figure 4 shows IMS spectra recorded when a pulse of $CHCl_3$ was injected to the drift gas. The interval between the spectra was 340 ms. The sharp peak at zero drift time is due to the electrons that were able pass through the drift tube without being captured. The small peak at 10 ms is due to the $Cl^-$ ions that are formed before the shutter grid. They all have to spend the same amount of time to reach the collector. Thus, for all spectra, this peak appears at the same time. However, the broad sample peak, because of the ions that are formed inside the drift region, shifts and broadens. The shape, as predicted by theory, is bell-

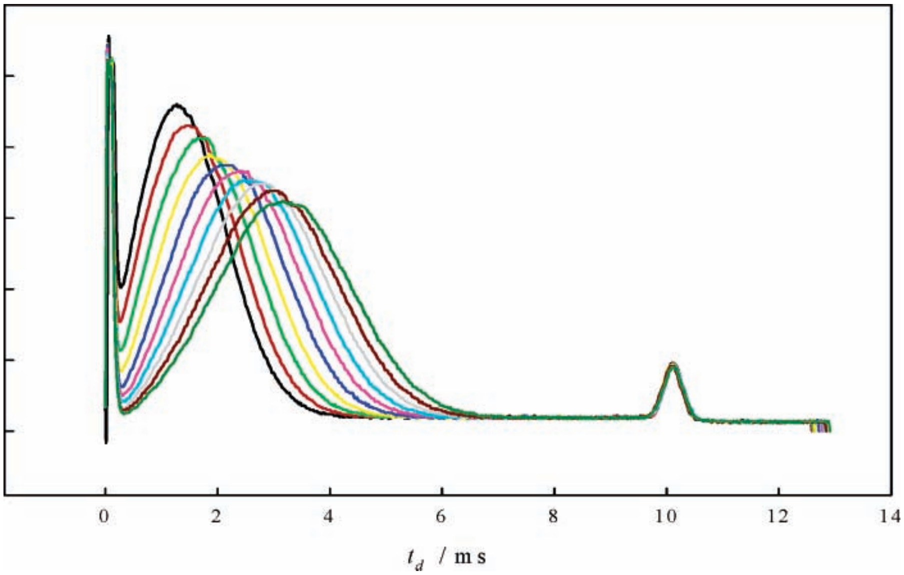

**Figure 4.** Ion mobility spectrometry (IMS) spectra that resulted from the injection of $CHCl_3$ as a pulse into the drift gas. The time interval between the spectra is 340 ms. Because the sample was introduced from the detector side, it appeared in shorter drift time and gradually shifted to longer drift times.

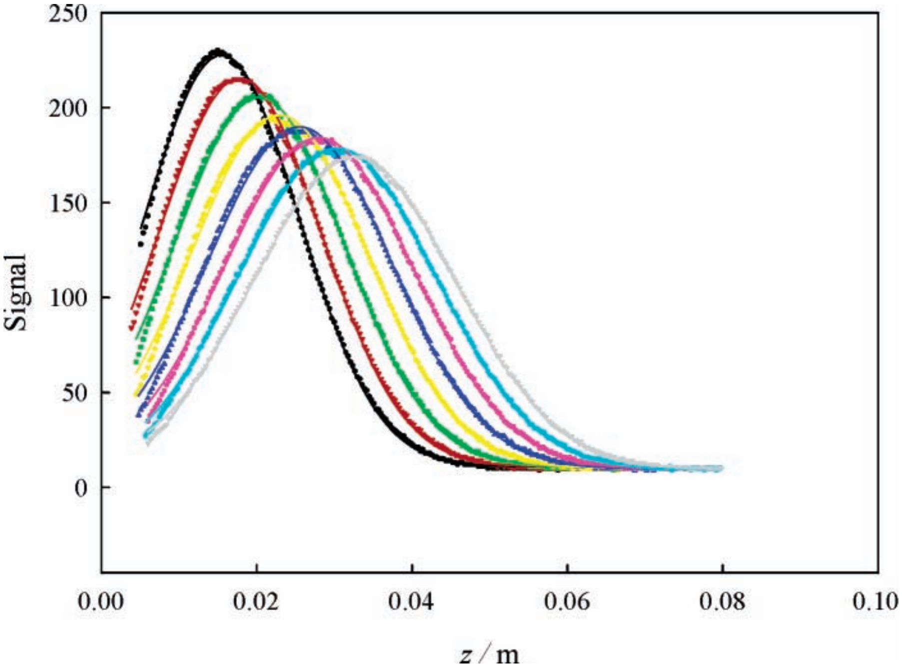

**Figure 5.** Experimental (symbols) and simulated spectra (lines) of $CHCl_3$ using the fitting parameters extracted from eq 8.

shaped and it appears from zero drift time and moves toward the longer drift time, because the sample cloud enters the drift tube from the collector side and gradually moves away from the collector. After background correction, the useful portion of the spectra was fitted into a function that is similar to eq 8:

$$\text{signal intensity} = \frac{\beta}{\sqrt{\chi}} \exp\left[-\frac{(z - z_0)^2}{4\chi}\right] \qquad (14)$$

where $\beta$ is a constant and $\chi = D_{12}t$. The results are shown in Figure 5. Note that the IMS spectra are expressed in time coordinates, whereas eq 8 is expressed in spatial coordinates. The drift time can be easily converted to $z$-coordinates using $z = vt$, where $v$ is the ion drift velocity, which is determined from the drift time of the $Cl^-$ ion peak (the peak at 10 ms) and the drift length.

The values of $\chi$ for each spectrum at a specific exposure time $t$ were extracted from the fit. Obviously, $\chi$ is a linear function of $t$ with a slope of the diffusion coefficient. In fact, the diffusion coefficient is proportional to the variance of the Gaussian peak. Figure 6 shows the plot of $\chi$ vs $t$, which is a straight line with $r^2 > 0.999$. From the slope of the line, the diffusion coefficient for chloroform was measured to be $0.22 \pm 0.01$ cm$^2$/s at 33 °C and 635 Torr.

Attempts were made to use eq 12 to fit the data, but the results were the same as those obtained from eq 8. The reason is that the corona discharge generates a very large electron flux. The electron current is $10^6$ times greater than that of the conventional $^{63}$Ni source.[22] In fact, the number of electrons, with respect to the number of sample molecules, is so high that only a small portion of electrons is consumed. In practice, the electron signal intensity was ~1000 times greater than that of the ions.

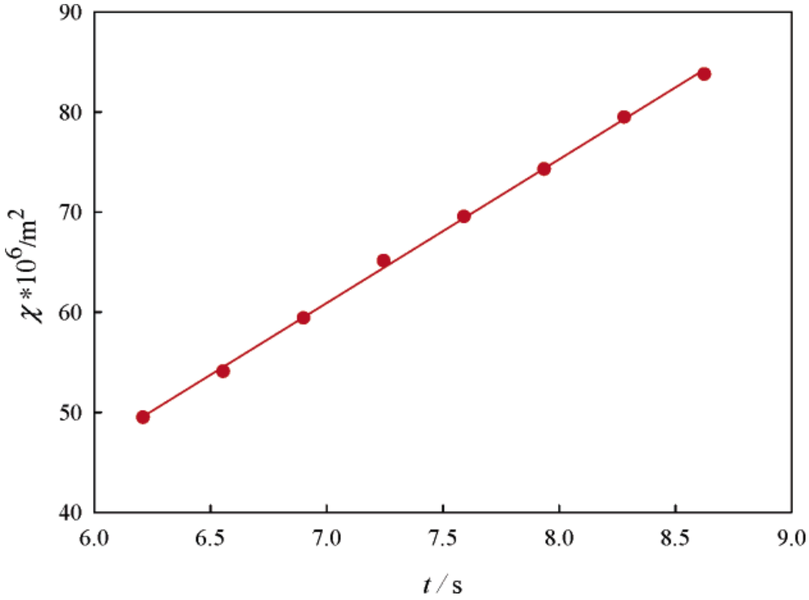

**Figure 6.** Plot of $\chi$ defined in eq 14 against the exposure time; the slope of the line gives the diffusion coefficient.

Therefore, it can be assumed that the electron concentration was almost constant and eq 8 is applicable.

This procedure was repeated for other compounds. The results and a comparison with other literature values are provided in Table 1. To enable an equivalent comparison, our data had to be converted to the pressures and temperatures at which reported data existed. This was achieved using the relation[24]

$$\frac{D_2}{D_1} = \frac{p_1}{p_2} \times \left(\frac{T_2}{T_1}\right)^2 \qquad (15)$$

The idea behind using this equation was that, in Chapman–Enskog theory, the diffusion coefficient is proportional to temperature and pressure as follows:

$$D \propto \frac{T^{3/2}}{\Omega}\left(\frac{1}{p}\right) \qquad (16)$$

where $\Omega$ is the cross section, which is proportional to $T^{-1/2}$. Clearly, the IMS results for the diffusion coefficients are in good agreement with those measured using GC techniques.

## VI. Conclusion

A new method was proposed for measuring the diffusion constant in a gas phase. The method is simple and inexpensive, and the results are in good agreement with accepted methods. This method monitors the movement of a molecular cloud and the changes in its concentration profile in real time nondestructively without any distraction. It is fast enough to observe the diffusion process in a gas phase. Although the proposed method is described in one dimension, one may design a wide electron beam in combination with a two-dimensional array of collectors to monitor the behavior of a cloud in three dimensions. This design can be even used in real-time monitoring of turbulence. However, the method is limited to the diffusion of compounds with high electron affinity diffusing in gases with very low electron affinity.

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## References and Notes

(1) Marrero, T. R.; Mason, E. A. *J Phys. Chem. Ref. Data* **1972**, *1*, 3.
(2) Cussler, E. L. *Diffusion Mass Transfer in Fluid Systems*, Second Edition; Cambridge University Press: New York, 1997.
(3) Jost, W. *Diffusion in Solids, Liquids, Gases*, Third Edition; Physical Chemistry: A Series of Monographs, Vol. 1; Academic Press: New York, 1960.
(4) Huang, T. C.; Yang, F. J. F.; Huang, C. J; Kuo, C. H. *J. Chromatogr.* **1972**, *70*, 13.
(5) Giddings, J. C.; Seager, S. L. *J. Chem. Phys.* **1960**, *33*, 1579.
(6) Maynard, V. R.; Grushka, E. *Adv. Chromatogr.* **1975**, *12*, 99.
(7) Katsanos, N. A.; Karaiskakis, G.; Vattis, D.; Lycourghiotis, A. *Chromatographia* **1981**, *14*, 695.
(8) Pathak, B. K.; Singh, V. N.; Singh, P. C. *Can. J. Chem. Eng.* **1981**, *59*, 362.
(9) Katsanos, N. A.; Karaiskakis, G. *J. Chromatogr.* **1983**, *254*, 15.
(10) Mueller, C. R.; Cahill, R. W. *J. Chem. Phys.* **1964**, *40*, 651.
(11) Ney, E. P.; Armistead, F. *Phys. Rev.* **1947**, *71*, 14.
(12) Winn, E. B. *Phys. Rev.* **1950**, *80*, 1024.
(13) Reus, K. W.; Zawakhals, C. J.; Smith, J. A. *Physica C* **1980**, *100*, 221.
(14) Zwakhals, C. J.; Reus, K. W. *Physica C* **1980**, *100*, 231.
(15) Plumb, I. C.; Ryan, K. R. *Int. J. Chem. Kinetics* **1983**, *15*, 1081.
(16) Taylor, G. *Proc. R. Soc. (London)* **1953**, *219*, 186.
(17) Taylor, G. *Proc. R. Soc. (London)* **1954**, *225*, 473.
(18) Aris, R. *Proc. R. Soc. London A* **1956**, *235*, 67.
(19) Albright, J. G.; Miller, D. G. *J. Phys. Chem.* **1980**, *84*, 1400.
(20) Rashidnia, N.; Balasubramaniam, R. *Appl. Opt.* **2002**, *41*, 1337.
(21) Hoo, Y. L.; Jin, W.; Ho, H. L.; Wang, D. N. *IEEE Photonics Technol. Lett.* **2003**, *15*, 1434.
(22) Tabrizchi, M.; Abedi, A. *Int. J Mass Spectrom.* **2002**, *218*, 75.
(23) Weisstein, E. W. *The CRC Concise Encyclopedia of Mathematics*; CRC Press: Boca Raton, FL, 1999.
(24) Hirschfelder, J. O.; Curtiss, Ch. F.; Bird, R. B. *Molecular Theory of Gases and Liquids*; Wiley: New York, 1954.