TABLE III. Lattice sum of triple-dipole interaction for several crystal structures. The quantities A and B are defined in Eq. (5).

Lattice	A	B
hcp	19.188 ± 0.008	6.784
fcc	19.184 ± 0.008	6.783
bcc	14.77 ± 0.02	6.738
sc	6.617 ± 0.003	6.617

over a wide range of densities. Thus, the triple-dipole term represents only about 2% of the binding energy of liquid He^4 at the equilibrium density. Since the three-body contribution is of such a small magnitude, we feel that the estimates we have obtained should be accurate enough to be used for most calculations, since the uncertainty in them should produce a negligible error in the total energy.

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PHYSICAL REVIEW A VOLUME 3, NUMBER 3 MARCH 1971

Tests of the Wannier Expressions for Diffusion Coefficients of Gaseous Ions in Electric Fields*

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All of the published experimental values of longitudinal and transverse diffusion coefficients of gaseous ions in electric fields, except those cases dominated by resonant charge transfer, are compared with the predictions of Wannier's theory. The products of the measured coefficients and the gas number density appear to vary as $v_d^3(E/N)^{-1}$, where v_d is the ionic drift velocity, in agreement with Wannier's predictions. Here E/N is the ratio of the electric drift field intensity to the gas number density. In addition, the absolute agreement between experiment and theory is quite satisfactory.

I. INTRODUCTION

If a tenuous cloud of ions of a single species is released in a gas throughout which a weak uniform electric field is applied, a steady flow of the ions along the field lines will develop, superimposed upon the much faster random motion which leads to diffusion. The velocity of the center of mass of the ion cloud, or equivalently, the average velocity of the ions, is called the drift velocity $\vec{v}_d$ and this velocity is directly proportional to the electric field intensity $\vec{E}$ provided that the field is kept weak. Thus,

$$\vec{v}_d = K\vec{E} , \tag{1}$$

where the constant of proportionality K is called the (scalar) mobility of the ions. A simple relation, known as the Einstein equation,[1] exists between the mobility and the diffusion coefficient D which is also a scalar:

$$K = eD/kT \ . \qquad (2)$$

Here e is the ionic charge, k is the Boltzmann constant, and T is the absolute gas temperature. Equation (2) is valid only when E is sufficiently weak that the ions are close to being in thermal equilibrium with the gas molecules, that is to say, when "low-field" conditions obtain. Under these conditions, the ionic velocity distribution is very nearly Maxwellian. The ionic motion is largely the random thermal motion produced by the heat energy of the gas, with a small drift component superimposed in the direction of the applied field.

If E is now raised to a level where the ions acquire an average energy appreciably in excess of the thermal energy of the gas molecules, a number of complications arise. The thermal energy becomes of less importance, but there are two large components of motion produced by the drift field: a directed component along the field lines, and a random component representing energy acquired from the drift field but converted into random form by collisions with molecules. The mobility K appearing in (1) is no longer a constant in general, but will usually depend upon the ratio of E to the gas number density N. The parameter E/N determines the average ionic energy gained from the field in steady-state drift, above the energy associated with the thermal motion. In addition, the energy distribution of the ions becomes non-Maxwellian and cannot be calculated accurately by existing theory. Furthermore, the rate of diffusion transverse to the field direction is different from that in the direction of the electric field, so that the diffusion coefficient becomes a tensor rather than a scalar. The diffusion coefficient tensor has the form

$$\overleftrightarrow{\mathrm{D}} = \begin{vmatrix} D_T & 0 & 0 \\ 0 & D_T & 0 \\ 0 & 0 & D_L \end{vmatrix} , \qquad (3)$$

where D_T is the (scalar) transverse diffusion coefficient which describes the rate of diffusion in directions perpendicular to $\vec{\mathrm{E}}$, and D_L is the (scalar) longitudinal diffusion coefficient characterizing diffusion in the field direction.[2] In the "intermediate-field" and "high-field" regions described here, there is no known simple relationship such as (2) between the mobility and diffusion coefficients.

The measurement of both mobilities and diffusion coefficients is complicated in most cases by chemical reactions occurring between the ions and gas molecules, even in very pure gases.[3] However, if a drift-tube mass spectrometer is employed for the measurements, and if a careful time analysis of the ions reaching the detector is carried out, reliable data on ions of known molecular composition can be obtained even in reacting systems.[3] The measurement of mobilities is comparatively simple, since all that is required is a determination of a properly defined average time of transit through the drift tube. Mobility data of an accuracy between 0.5 and 4% are available for many mass-identified ions in various gases. The measurement of diffusion coefficients is much more difficult, because here a spatial or temporal distribution function must be determined. Reliable diffusion coefficients for ions of known composition have only recently become available. These data are few in number and are much less accurately known than are the mobilities, in general.

II. THEORY

Most of what is known on the theoretical side about the motion of gaseous ions in strong electric fields is due to Wannier, who in 1953 published a monumental paper on this subject.[2] One of Wannier's accomplishments was the derivation of high-field equations for D_L and D_T based on the solution of the Boltzmann equation for two different scattering models. In one model, the scattering was assumed to be dominated by the polarization force between an ion and a neighboring molecule. This force gives rise to a constant mean free time between collisions. The other model added to the assumption of constant mean free time that of isotropic scattering. The results for the two models do not differ appreciably, which is as expected since polarization scattering is very nearly isotropic. Wannier's equations (151) and (152) for the isotropic scattering model may be put into the following convenient form:

$$D_T(E) = D(0) + \zeta_T \left[\frac{mM}{m+M} \right] \frac{v_d^3}{eE} \ , \qquad (4)$$

$$D_L(E) = D(0) + \zeta_L \left[\frac{mM}{m+M} \right] \frac{v_d^3}{eE} \ , \qquad (5)$$

where

$$\zeta_T = \frac{1}{3} \frac{(M+m)^2}{m(M+2m)} \ , \qquad (6)$$

$$\zeta_L = \frac{1}{3} \frac{(M+m)(M+4m)}{m(M+2m)} \ . \qquad (7)$$

Here $D(0)$ is the zero-field value of D, which can be calculated from the measured value of v_d by the Einstein equation. The mass of the ion is denoted by m, that of the molecule by M. As expected,

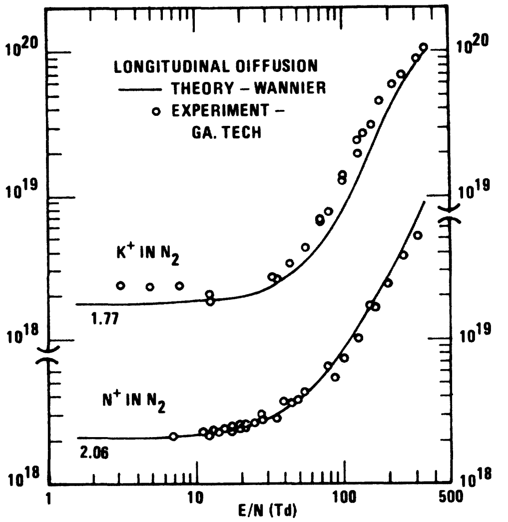

FIG. 1. Experimental results on longitudinal diffusion of N$^+$ and K$^+$ ions in N$_2$ at room temperature, compared with the predictions of Wannier's theory. N is the gas number density and D_L is the longitudinal diffusion coefficient. E/N is measured in townsends (1 Td = 10^{-17} V cm^2).

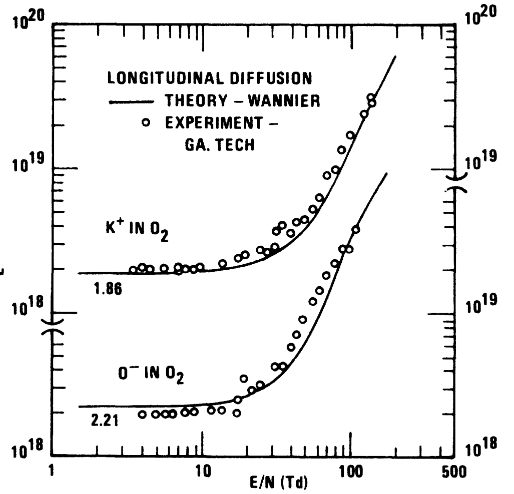

FIG. 2. Experimental results on longitudinal diffusion of O$^-$ and K$^+$ ions in O$_2$ at room temperature, compared with the predictions of Wannier's theory. N is the gas number density and D_L is the longitudinal diffusion coefficient. E/N is measured in townsends (1 Td = 10^{-17} V cm^2).

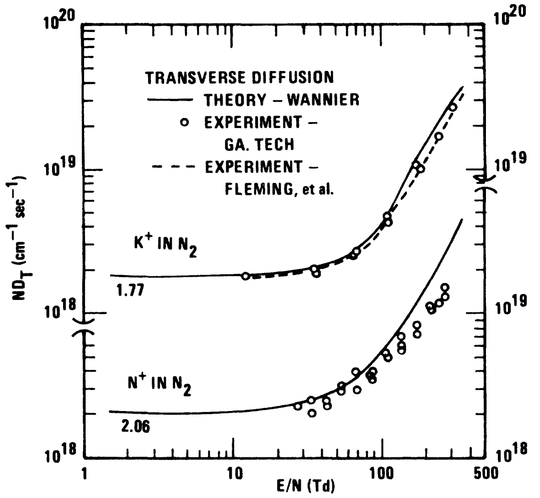

FIG. 3. Experimental results on transverse diffusion of N$^+$ and K$^+$ ions in N$_2$ at room temperature, compared with the predictions of Wannier's theory. N is the gas number density and D_T is the transverse diffusion coefficient. E/N is measured in townsends (1 Td = 10^{-17} V cm^2).

$ND(E)$ depends on E and N only in the combination E/N. These equations predict that $D_L > D_T$ and that both ND_L and ND_T should vary as $v_d^3(E/N)^{-1}$ at high E/N. Wannier's equations were phrased in terms of the mean free time τ rather than v_d. However, τ and v_d are related by the equation

$$v_d = \xi \left[1 + \frac{m}{M}\right]\left[\frac{eE}{m}\right]\tau , \tag{8}$$

where ξ is a factor of order unity that depends in a complicated way on the ion-molecule force law and the masses m and M. The factor ξ has not been explicitly evaluated for realistic models of ion-molecule combinations. Equation (8) with $\xi = 1$ was used to obtain Eqs. (4)–(7) from Wannier's equations. Equations (4) and (5) can be used for direct comparisons with experiment because v_d has been measured as a function of E/N for all of the ions for which diffusion coefficient data are available. However, no test of the Wannier predictions appears to have been made before the one described in Sec. III.

III. COMPARISON OF EXPERIMENT WITH THEORY

Experimental data on diffusion coefficients of ions in nitrogen, oxygen, and hydrogen at room temperature are now available for comparison with the predictions of Eqs. (4) and (5). Comparisons are made in Figs. 1–4. The data labeled "Ga. Tech" were obtained with a drift-tube mass spectrometer, and the identity of the ions is certain. Furthermore, it is known that only a single species of ion was involved in each measurement. The remaining data were obtained with drift tubes lacking mass spectrometers, but there is little doubt concerning the identities of the ions in the data shown. The units of E/N on the abscissas are the townsend (Td), where 1 Td = 10^{-17} V cm^2. The number at the left-hand side of each curve is the value of $D(0)$ calculated

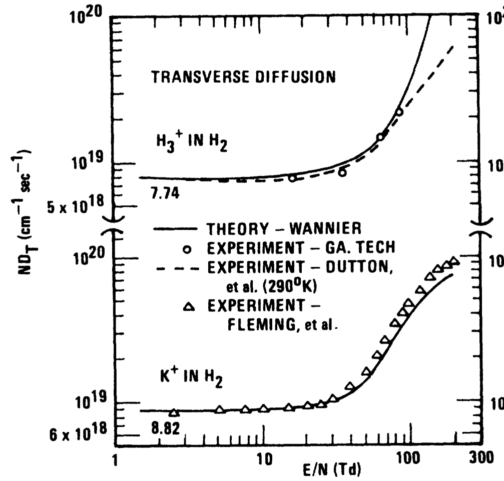

FIG. 4. Experimental results on transverse diffusion of K^+ and H_3^+ ions in H_2 at room temperature, compared with the predictions of Wannier's theory. N is the gas number density and D_T is the transverse diffusion coefficient. E/N is measured in townsends ($1\ \mathrm{Td} = 10^{-17}\ \mathrm{V\,cm^2}$).

from the measured low-field mobility by the Einstein equation (2). In Fig. 1, the experimental data are those of Moseley *et al*[4]; the experimental data in Fig. 2 are those of Snuggs *et al.*[5] The "Ga. Tech" experimental data in Fig. 3 were taken from papers by Mosley *et al.*[4,6,7]; the other experimental data in this figure are those of Fleming *et al.*[8] In Fig. 4, the data labeled "Ga. Tech" are those of Miller *et al.*[9]; the other data are from papers by Dutton *et al.*[10] and Fleming *et al.*[11] Skullerud[12] has also published D_T data for ions in H_2 – they are not plotted in Fig. 4. Skullerud's values were originally thought to apply to the H_3^+ ion, but are now believed to refer to an impurity ion[13] present because his apparatus was not bakeable. Skullerud's data rise much less sharply with increasing E/N than do the H_3^+ data shown in Fig. 4. The values of v_d used in plotting Wannier's predictions in Figs. 1–4 were taken from the papers by the Ga. Tech group,[4–7,9] except for the values used in the K^+ in H_2 calculation which were taken from Fleming *et al.*[11]

It may be of interest to point out that the values of D_L obtained by the Ga. Tech group were measured by a technique completely different from that which they used to determine D_T. Furthermore, the technique employed by the Ga. Tech group for obtaining D_T was completely different from that used by the other groups for measuring this quantity.

Experimental diffusion coefficient data are also available for N_2^+ in N_2 and for O_2^+ and O_2^- in O_2.[5–7] These data are not shown, however, because the motion of these ions in the indicated gases is known to be dominated by resonant charge transfer and would not be expected to agree with the predictions of the Wannier analysis, which did not take this scattering mechanism into account.

IV. CONCLUSIONS

In Figs. 1–4, the basic agreement between the experimental data and Wannier's theoretical predictions is evident, although the agreement in absolute magnitude is not close in all cases. However, when one considers the approximate nature of the theory, the assignment of a value of unity to ξ for all calculations made in preparing the figures, the wide range of ion-molecule systems considered, and the rather large probable errors (up to 25%) in the measured values, the absolute agreement is certainly satisfactory. In fact, excellent fits can be obtained for all curves by a small adjustment in ξ. The values of ξ for a best fit, given in Table I, vary from unity by no more than 20%.

The variation of the ND product as $v_d^3(E/N)^{-1}$ has been predicted for ion-molecule interactions other than the constant mean free time, isotropic scattering model on which Eqs. (4)–(7) are based. Wannier[2] also predicts such a dependence for polarization scattering. Further, Skullerud[14] predicts that in general for a constant collision cross section ND_L will be proportional to $v_d^3(E/N)^{-1}$.

These predictions and the measurements presented here are in disagreement with a recent contention by Varney[15] that the observed values of D_L reported in Refs. 4–7 are not diffusion coefficients at all. Varney's error, which is discussed in detail by Gatland and McDaniel,[16] lies in assuming that diffusion and the random walk motion of the ions are unrelated. Varney also predicts that the measured "apparent" values of ND_L should increase as v_d^2 due to this random motion. This prediction agrees with Eq. (5) only if v_d varies linearly with E/N. In fact, at high E/N, v_d is observed to vary in different ways with E/N for different ion-molecule systems.[17] The high-field variation is as $(E/N)^{1/2}$ in many cases.

Note added in proof. The practical significance of the agreement between the experimental data and

TABLE I. Values of ξ which produce the best fit in Figs. 1–4.

Ion-gas combination	Diffusion coefficient	ξ
N^+ in N_2	D_L	1.03
	D_T	1.2
K^+ in N_2	D_L	0.9
	D_T	1.03
O^- in O_2	D_L	0.92
K^+ in O_2	D_L	0.94
H_3^+ in H_2	D_T	1.0
K^+ in H_2	D_T	0.92

Wannier's predictions which has been established here is connected primarily with the use of drift tubes for the measurement of rate coefficients for ion-molecule reactions. In such measurements, the effects of longitudinal and transverse diffusion of the ions should be considered, but the diffusion coefficients above the thermal region are known for only a few ionic species. When the necessary coefficients are not available, the Wannier equations may be used to calculate values of D_L and D_T which should be at least approximately correct, except for cases where resonant charge transfer occurs.

ACKNOWLEDGMENT

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Quantum-Electrodynamic Treatment of Spontaneous Emission in the Presence of an Applied Field*

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Spontaneous emission by a "two-level atom" interacting with a highly excited field mode is described using quantum electrodynamics without time-dependent perturbation theory. It is found that both the line shape and the Lamb shift are affected by the "applied field." Detailed solutions are presented as a function of the population of the "applied-field mode" and as a function of the detuning.

I. INTRODUCTION

There have been a number of treatments of the phenomena which occur when spontaneous and stimulated emission proceed simultaneously in the same population.[1-6] These treatments have used various forms of semiclassical radiation theory. Two papers in particular give an extensive treatment using a form of semiclassical theory which includes the effects of radiation reaction on the radiating atom.[5,6]

These improved semiclassical theories have predicted certain nonlinear effects which occur when spontaneous and stimulated emission occur simultaneously in the same population.[5,6] These effects involve changes in the line shape and in the radiative frequency shift, as well as various transient