[‡] Submitted by F. H. Gertler in partial fulfillment of the requirements for the degree of Doctor of Philosophy at New York University.

[§] Present address: Physics Department and Space Sciences Laboratory, University of California, Berkeley, California.

[1] L. Spruch and L. Rosenberg, Phys. Rev. 116, 1034 1959).

[2] L. Rosenberg, L. Spruch, and T. F. O'Malley, Phys. Rev. 118, 184 (1960).

[3] E. A. Hylleraas and B. Undheim, Z. Physik 65, 759 (1930).

[4] R. Jost and A. Pais, Phys. Rev. 82, 840 (1951).

[5] V. Bargmann, Proc. Natl. Acad. Sci. U. S. 38, 961 (1952).

[6] J. Schwinger, Proc. Natl. Acad. Sci. U. S. 47, 122 (1961).

[7] L. Spruch, in *Lectures in Theoretical Physics*, edited by W. E. Brittin, J. Downs, and W. B. Downs (Interscience Publishers, Inc., and John Wiley & Sons, Inc., New York, 1962, Vol. IV, p 161 (see especially pp. 196-9) .

[8] L. Spruch, in *Proceedings of the Ninth Summer Meeting of Nuclear Physicists, Hercegnovi*, 1964, edited by M. Cerineo, (Federal Nuclear Energy Commission of Yugoslavia, Belgrade, 1965) , Vol. I, p. 271. This paper also contains a review of earlier work on necessary conditions for the existence of bound states.

[9] K. O. Friedrichs, *Studies and Essays Presented to R. Courant* (Interscience Publishers, Inc., New York, 1948), p. 145.

[10] T. Kato, Math Ann. 162, 258 (1966)

[11] H. Feshbach, Ann. Phys. (N. Y.) 5, 537 (1958); *ibid.* 19, 287 (1962).

[12] Y. Hahn and L. Spruch, Bull. Am. Phys. Soc. 12, 560 (1967), and to be published.

[13] L. Wolniewicz, J. Chem. Phys. 41, 1646 (1964); J. D. Stuart and F. A. Matsen, J. Chem. Phys. 43, 1087 (1965).

[14] A. A. Frost, M. Inokuti, and J. P. Lowe, J. Chem. Phys. 41, 482 (1964).

[15] D. R. Bates, K. Ledsham, and A. L. Stewart, Phil. Trans. Rcy. Soc. (London) *A*246, 215 (1954); H. Wind, J. Chem. Phys. 42, 2371 (1965).

[16] A. S. Wightman, Phys. Rev. 77, 521 (1950); R. F. Wallis, R. Herman, and H. W. Milnes, J. Mol. Spectry. 4, 51 (1960).

[17] D. R. Bates and T. R. Carson, Proc. Roy. Soc. (London) A234, 207 (1956).

[18] W. Kolos and L. Wolniewicz, J. Chem. Phys. 43, 2429 (1965).

Resonance Scattering and the Drift Motion of Electrons through Gases*

Lothar Frommhold
Physics Department and Electronics Research
Center, University of Texas, Austin, Texas

(Received 16 February 1968; revised manuscript received 29 March 1968)

Density-dependent values of the electron drift velocity in hydrogen, deuterium, and nitrogen gas have recently been reported. Their reciprocal values are shown to be a linear function of the gas density. Several possible theoretical explanations are discussed, some of which lead to such a linear pressure dependence. It is concluded that electron trapping by some low-energy resonance states is likely to take place. "Rotational resonances" in atom-rotator scattering have been described in a theoretical paper by Kouri, and it is thought that rotational resonances should be observed in electron-molecule scattering as well, at electron energies close to thermal energy. At the higher electron energies (≃1 eV), the known "single-particle" resonance states of H_2 and N_2 near 2 eV are probably responsible for the delay in the electron motion at high densities.

INTRODUCTION

According to the well-known theories of the drift motion of electrons through gases,[1,2] the electron drift velocity v_e should be a function of the ratio of electric field to pressure, E/p, of the gas temperature T, and of the nature of the gas, but not of its density. Recently, however, in very accurate measurements of the electron drift velocity in gases, a dependence upon the neutral density was found. Lowke[3] was able to show that in nitrogen, at low temperatures and varying densities up to 7×10^{19} cm^{-3}, electron drift velocities decrease slightly (by 3%) with increasing densities. Grünberg[4] found similarly, at room temperatures and at higher densities in hydrogen and nitrogen, drift velocities decreasing with increasing densities. Variations of v_e in hydrogen of up to 30% for neutral densities up to 10^{21} cm^{-3} have been reported in this experiment.[4] In deuterium gas at 77°K, density-dependent drift velocities of electrons have also been reported.[5]

The reason for the observed density dependences is not clear, although the fact that such a dependence exists is not really surprising. Several possible reasons have been mentioned in the past and will be reviewed here, after the experimental evidence is presented in a new form.

Since several theoretical considerations to be discussed suggest that the inverse drift velocity depends linearly upon the gas density, the reciprocals of the experimental drift velocity values[3–5] are plotted as function of their neutral densities. The result is in every case a straight line, an arbitrary selection of which is shown in Fig. 1. (Here, as in the following, pressures rather than densities are used to describe the density dependence. Corrections of the pressure readings have been made,[3,4] however, such that p becomes a linear function of the density, $n = 3.5 \times 10^{16} p$ cm^{-3} (where p is in Torr). All pressure readings are reduced to 300°K.) From these plots it appears that the drift velocities obey a relation of the form

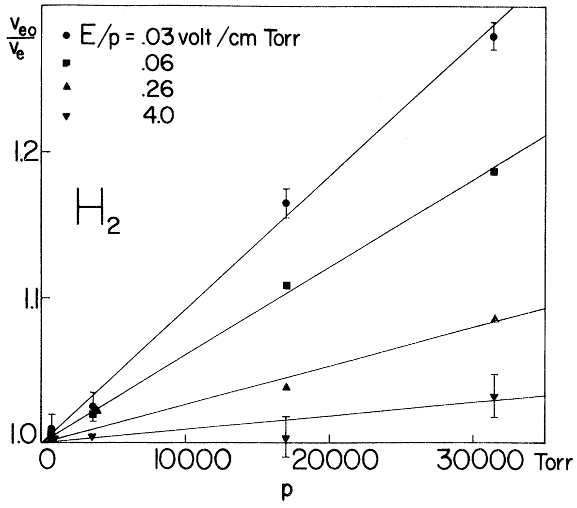

FIG. 1: A selection of experimental reciprocal drift velocities, v_{e0}/v_e, versus the hydrogen pressure. As in this graph, a linear dependence is accurately observed for all the existing data.[3–5] (No linear dependence of v_e versus p could be obtained at the larger density ranges of Ref. 4.) Their slopes α are plotted in Fig. 2, as function of the characteristic electron energies and gas temperature, and will be called $(\nu\tau)_1$ for reasons explained below. (Data from Ref. 4)

$$v_e = v_{e0}/(1 + \alpha p), \qquad (1)$$

if E/p and T are kept constant. Hence v_{e0} is the "zero-density" value of the drift velocity, and α/v_{e0} is the slope of the $1/v_e$-versus-p curve. α has the dimensions of Torr^{-1}. When possible, it is determined by the method of least squares. The resulting α values are plotted in Fig. 2 as functions of the "characteristic energies"[5,6] of the electrons. This energy eD/μ is a function of T and E/p, and is equal to kT for zero field strengths. (D is the diffusion coefficient, μ the mobility and e the charge of an electron.)

From the data in Ref. 4, for hydrogen at 300°K and nearly thermal electrons, α is found to be about 9×10^{-6} Torr^{-1}. It decreases monotonically to nearly 0.6×10^{-6} Torr^{-1}, at the highest mean electron energy of 0.6 eV. This result is consistent with the findings in Ref. 3, where no such pressure dependence could be detected. The highest pressures employed were 500 Torr in Ref. 3 and more than 30,000 Torr in Ref. 4. Hence, in Ref. 3, the resulting variations of v_e were small fractions of 1% and thus unresolvable. Only Grünberg's data[4] can be used to derive α.

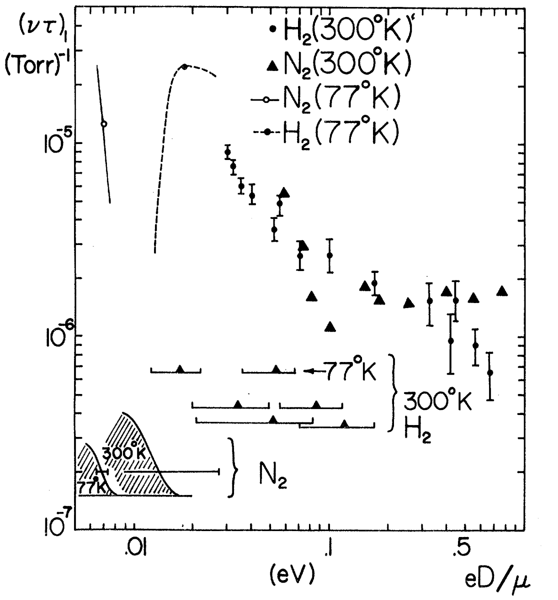

FIG. 2: The slopes $\alpha = (\nu\tau)_1$ of the experimental v_{e0}/v_e versus p curves (as in Fig. 1) for hydrogen and nitrogen at 77 and 300°K, as function of the characteristic electron energy. (The curve for hydrogen at 77°K is somewhat schematic.) In a schematic way, the significant rotational resonance levels and their widths are indicated for each gas and temperature.

For hydrogen at 77°K and thermal electrons (≈ 7 meV), no pressure effect was found. From Lowke's data we estimate that in this case α does not exceed $(2-5) \times 10^{-6}$ Torr^{-1} and is probably much smaller than this value. This is surprising because Crompton *et al.*[5] found in deuterium, at thermal energies and 77°K, a rather strong effect, $\alpha \simeq (8-10) \times 10^{-6}$ Torr^{-1}. At the same time these authors[5] confirm Lowke's results about the near absence of a pressure effect in hydrogen, a noteworthy point to which we shall come back below. At increased mean electron energies in hydrogen, though, Lowke's data indicate some pressure dependence near 15 meV, in agreement with the recent work by Crompton *et al.*[5] The inferred α value is $\alpha \simeq 10 \times 10^{-6}$ Torr^{-1} (which could be in error by 50%). This situation is indicated schematically in Fig. 2. In deuterium,[5] the α values do not change much for energies between 6 and 14 meV $[\alpha \simeq (8-10) \times 10^{-6}$ Torr$^{-1}]$ and seem to fall off to 30–50% of this value with increasing energies, between 15 and 20 meV. Grünberg[4] has not reported results at 77°K.

For nitrogen at 300°K and nearly thermal electrons, Grünberg's data[4] indicate large α values, which fast approach a nearly constant value of $(1-2) \times 10^{-6}$ Torr^{-1} with increasing energies. At 77°K, Lowke[3] reported a similar pressure effect, as indicated in Fig. 2.

It is the purpose of this paper to propose an interpretation of all these data. There are several possible effects of high densities on the drift motion, which will be discussed in the subsequent sections.

ELECTRON TRAPPING

In previous papers dealing with the drift motion of electrons through gases, mention has been made that electron trapping could efficiently slow down the drift motion of electrons in an electric field,[7–10] particularly if the densities are high. For the present purpose, a trapped electron is an electron captured by a gas molecule, which then becomes a negative ion. Negative ions are known to move much more slowly than electrons, because of their large mass. A negative ion can decompose after some lifetime τ, either by collisional electron detachment,[8,10,11] or collisionlessly, if it is a short-lived compound or resonance state.[12–15] If an electron is trapped and released many times while drifting through a gas, it will be increasingly delayed as the densities are increased. Hence the mean or "apparent" drift velocities v_e will be smaller than the "zero-density" drift velocity v_{e0}, which is the averaged velocity of an electron between two trapping collisions. It has been shown that the relation between v_e and v_{e0} is given by

$$v_e = v_{e0}/(1+\nu\tau), \qquad (2)$$

where ν is the collision frequency of trapping collisions and τ the mean time an electron remains trapped in such a collision, or the mean lifetime of a trapped electron. Eq. (2) can be found in Refs. 8, 11, and in the work of Ritchie and Turner,[16] and a short proof is given in the appendix. It is valid if both $1/\nu$ and τ are small compared to the time of flight of the electrons in the drift tube. v_{e0} in Eq. (2) is, according to our definition, not pressure-dependent if E/p and T are constant, and any pressure dependence of v_e must be due to the product $\nu\tau$.

The mean frequency of trapping collisions can be expressed in terms of the two-body attachment, or resonance cross section (whichever applies), according to[1,2]

$$\nu = n\int q_r(2\epsilon/m)^{\frac{1}{2}} f(\epsilon,\bar{\epsilon})d\epsilon. \qquad (3)$$

Here n is the neutral density, m the electron mass, $\bar{\epsilon}$ the characteristic or mean energy (which is a function of E/p and T), and $f(\epsilon,\bar{\epsilon})$ is the distribution function of the electron energies ϵ. In this case, ν is proportional to the pressure for constant E/p and T. Should a three-body attachment reaction take place instead, the attachment rate ν will be proportional to p^2, the square of the pressure.[17,10]

(a) The lifetime τ of the trapped state is proportional to the inverse density, if collisional detachment takes place. Hence, for a two-body attachment and subsequent collisional detachment of the electron, v_e is different from v_{e0} because $\nu\tau \neq 0$. There is no pressure dependence of v_e, though, because the dependence of ν and τ cancel out. For the present purpose, this case of two-body attachment and collisional detachment is of no interest and is mentioned only for the sake of completeness.

(b) For a three-body attachment followed by collisional detachment, the reciprocal apparent drift velocity actually is a linear function of the pressure, as in Eq. (1), with $\alpha = (\nu\tau)_1$. The subscript 1 indicates that the product of ν and τ, which is proportional to p, was algebraically reduced to unit pressure, thus becoming density independent. This concept of three-body attachment and collisional detachment is obviously of no use for explaining the results of Fig. 2, too, although it leads to a pressure dependence of v_e consistent with the experiment. A theoretical argument has been advanced by Taylor *et al.*[15] that H_2^- should not exist as a stable ion, and the nonexistence of N_2^- has never been questioned. Hence it is felt that the collisional detachment hypothesis is not applicable here for hydrogen and nitrogen, and we turn our attention to the alternative: auto-ionizing negative ions or resonance states of molecules, which are known from electron-molecule scattering experiments and theories.[12–15]

(c) For resonance states, we should expect a lifetime τ which does not depend upon the density, since these states decay by virtue of their internal instability.[18] Only in the case of very high pressures, for neutral-neutral collision frequencies ν_0 comparable to or exceeding $1/\tau$, the lifetimes can be appreciably affected by neutral resonance-state collisions. Because τ is of the order of 10^{-13}–10^{-14} sec for most of the known molecular resonance states,[13–15] the corresponding critical hydrogen or nitrogen pressures at 300°K are many hundreds of atmospheres. At the lower densities of interest to us (up to 40 atm), the assumption of a pressure-independent τ appears still reasonable. Hence, for the "resonance scattering case," v_e turns out to be density dependent in the same way as the experimental data, because ν is proportional to the density.

The question here is whether such resonance states exist at these electron energies between thermal and about 1 eV energy. For hydrogen, the lowest known electron scattering resonance occurs at 2.3 eV, (a "single particle resonance"; see Ref. 14) with an estimated width of 1–3 eV.[15] Although this resonance could possibly account for values of $\alpha = (\nu_1\tau) = 10^{-6}$ Torr^{-1} at electron energies near 1 eV,[19] it is hard to see how this resonance could be responsible for increasing values of $(\nu_1\tau)$ for decreasing electron energies, down to 0.03 eV. For nitrogen, the situation is quite the same: the lowest known resonance state[13] is near 2.3 eV; at nearly thermal electron energies this resonance state should hardly be detectable.

We want to raise here the question whether, at the lower electron energies, the observed $(\nu_1\tau)$ values could be due to some other low-energy resonance states, which are hitherto undetected. In a paper by Kouri, it has been shown that in an atom-rigid-rotator collision, the first two (energetically unaccessible) rotator states have an effect on the open-channel wave functions.[20] These "rotational resonances" should be expected as well in electron-rotator scattering. Although, at the present time, everything which can be said about the rotational resonances for electron scattering must be speculative, it is felt that these states (if they exist) could definitely cause density-dependent drift velocities of electrons and ions. Therefore it is of some interest to discuss and estimate their effects on the measurements cited above.

In hydrogen, the lower rotational levels are given by $E_J = BJ(J+1)$, where[21] $B = 0.007\,56$ eV and $J = 0, 1, 2, \ldots$. Hence the relevant rotational levels above the rotational ground state are 15, 45, 90, and 150 meV. At 300°K gas temperature ($kT \simeq 25$ meV), the ground state and the lower two rotational states will be populated in the ratio 0.3: 0.45: 0.22, according to their statistical weights and the Boltzmann factor; the higher levels are practically not populated. Rotational resonances for a molecule in the Jth state occur at the two energy levels somewhat below the $(J+1)$th and $(J+2)$th rotational levels,[20] from which the energy of the Jth state is to be substracted; see Table I. The lifetimes of these states are probably a not too small fraction of their rotational periods; we take arbitrarily $\frac{1}{10}$ of it as an order-of-magnitude estimate, and compute their widths by means of these lifetimes and the uncertainty principle. These data are listed in Table I for the six resonance states of interest at a temperature of 300°K.

At the lowest mean electron energy considered here (≈ 30 meV), four of these resonance states are involved: one at 15, one at 30, and two at 45 meV; and at intermediate energies the higher ones are involved, too. At electron energies above 0.3 or 0.5 eV, all of these rotational resonance states should be fairly unimportant; at these energies, though, the very broad single-particle resonance at 2.3 eV comes into play.[19]

Although, with several resonance states being involved at the same time, the simple theoretical derivation of the drift velocity is not satisfactory,[22] it still gives the right pressure dependence, and an averaged value of $\nu_1\tau$. Thus, with the data of Table I, a "mean" cross section for the lower rotational states can be derived. For the lowest energies, we obtain $\bar{q}_r = (\nu_1\tau)/(nv\tau) \simeq 20\times10^{-16}$ cm^2, from the data in Fig. 2. For intermediate energies, 0.1–0.2 eV, nearly the same value is obtained because of the decreasing lifetimes. For the highest energies see Ref. 19. These cross sections are probably not wrong by more than an order of magnitude; in any case, they certainly do not appear to be unrealistic. This is considered to be a first success in our interpretation. Furthermore, we seem to understand the energy dependence of $\nu_1\tau$, or at least the fact of very large values of α at thermal energies, which decrease as the electron energy is increased in such a way that certain levels become less important, and which finally fall off to very small values at energies generally too large for all of these rotational resonances. (At these large energies, however, another known, very broad single-particle resonance comes into play.) We plotted these rotational levels in the lower half of Fig. 2 in order to demonstrate their relationships to the general shape of the $\nu_1\tau$-versus-$\bar{\epsilon}$ curve. We feel that (a) the realistic value of the derived cross section and (b) the semiquantitatively interpretable energy dependence of $\nu_1\tau$ are not likely to be merely accidental, and we take this as some indication that rotational resonances (here, in hydrogen) do exist. This conclusion will receive further confirmation from the interpretation of the other data below.

In hydrogen at 77°K, only the rotational states with $J = 0$ and 1 are occupied significantly, their relative abundance being 25 and 75%, respectively. Since the lowest rotational resonance level is near 15 meV, one should not expect a pressure effect at electron energies much below that energy, for example for thermal electrons (~7 meV). This expectation is in agreement with the experimental evidence. As the mean electron energies are increased to nearly 15 meV, a pressure effect should be expected if these rotational resonances are real and, indeed, large values of $\nu_1\tau$ are found from the experiment (see Fig. 2). These two predictions together with their experimental verifications appear to be a rather strong additional support for the assumed existence of the rotational resonance states.

For deuterium, the rotational constant B is half as large as for hydrogen.[21] The rotational levels of interest at 77°K are, in this case, 7.5, 15, 23, 38, and 53 meV. Hence, even for thermal electrons (~7 meV), a strong pressure effect is to be expected and experimentally found. The striking difference between the hydrogen and deuterium data[5] was mentioned above and can be

TABLE I. The hypothetical resonances in hydrogen.

Rotational state	level (meV)	Abundance at 300°K	Lower resonance state level (meV)	Lower resonance state width (meV)	Lower resonance state lifetime (10^{-14} sec)	Upper resonance state level (meV)	Upper resonance state width (meV)	Upper resonance state lifetime (10^{-14} sec)
$J=0$	0	0.30	15	10	2.5	45	30	0.8
$J=1$	17	0.45	30	30	0.8	75	60	0.4
$J=2$	51	0.22	45	60	0.4	106	100	0.25

explained with ease, if rotational resonances are assumed to exist.

One might think that in principle similar rotational resonances should affect the drift motion of *ions* in hydrogen as well, thus enforcing a pressure dependent ion drift velocity, too. However, the lifetimes of these ion-rotator scattering states should be of the same order as in Table I, and hence are not long compared to the interaction time for nonresonant ion-molecule scattering ($\approx 10^{-13}$ sec). Therefore, the effect of "ion trapping" could be largely masked.

For nitrogen of 300°K, the situation is more complex, because there are many more resonance states to consider. The rotational constant is[21] $B = 0.25$ meV; leading, at 300°K, to about 15 excited rotational states of significant population. Hence, about 30 rotational resonances should be of importance.[20] The lifetimes of the resonance states of the more important higher rotational levels (near 50 meV) are about 10^{-14} sec and their widths about 30 meV. The most significant difference to hydrogen is the high density of these levels near thermal energies. Their energies are about $2JB$ and $4JB$, respectively, or about 7 and 15 meV for the larger J's, and much less for the smaller J's. There are probably no such levels at higher energies,[20] which has the effect that at mean electron energies above ≈ 50 meV, not much trapping due to these states should be observed. And, indeed, we find from Fig. 2 rapidly decreasing values of $\nu_1\tau$ at energies of 60 and 70 meV, and a nearly constant value at energies above 0.1 eV, which, as in the hydrogen case, should be due to the broad single-particle resonance at ≈ 2.3 eV.[13]

At 77°K in nitrogen, one has about eight rotational states populated and thus about 16 significant rotational resonances to consider,[20] with energy levels up to about 8 meV. The lifetimes and widths are about 10^{-12} sec and 0.3 meV, respectively, in this case. Thus, at an electron energy of 8 meV (taken from Fig. 5 in Ref. 3), a large trapping effect is expected and observed; the cross section in this case is again equal to 20×10^{-16} cm^2, as in hydrogen.

For nitrogen and the larger electron energies, $\nu_1\tau$ can be estimated as follows. From recent measurements[23] of the total scattering cross section for electron–N_2 scattering, the resonance collision frequency ν_1 can be estimated by using Eq. (3), a Maxwellian energy distribution for the electrons, and a value q_r equal to the total[23] minus the nonresonant cross section, which we estimate from Ref. 23 to be about 6 Å^2. For the three electron energies of 0.25, 0.55, and 0.9 eV, we thus obtain the collision frequencies $\nu_1 = (0.3,\ 0.9,\ \text{and}\ 2.4) \times 10^9$ Torr^{-1} sec^{-1}. Hence an assumed lifetime τ of (6, 2, and 1)$\times 10^{-15}$ sec, respectively, would yield the correct value $\alpha = \nu_1\tau = 1.8 \times 10^{-6}$ Torr^{-1}. This lifetime is indeed an appreciable fraction of the vibrational period ($\cong 3 \times 10^{-14}$ sec for the ground state). It is felt that a more elaborate approach could probably explain the observed values of $\nu_1\tau$ (Fig. 2), under the assumption of a constant lifetime of some 10^{-15} sec duration. We conclude that the observed pressure effect of v_e, for electron energies between 0.1 and 1 eV, is definitely of an order of magnitude to be expected for the known single-particle resonance, whose cross section peaks near 2.3 eV.

Summarizing the discussion of the low-energy resonance states in hydrogen, deuterium, and nitrogen, it can be said that the assumption of rotational resonances seems to explain the experimental data very well, in a semiquantitative way. At increasing energies, the known single-particle resonances may be considered to be of increasing importance; their estimated effect on the drift motion of electrons is certainly of the observed order of magnitude.

DIMER FORMATION

There is still another possible explanation for such a linear pressure dependence of v_e, which does not resort to electron trapping. At high densities, there is experimental evidence that dimers exist—in H_2, for example,[24] the dimer $(H_2)_2$. Similar dimers exist in the gas phase for any other gas.[25] Dimers are formed according to the reaction $H_2 + 2H_2 \rightarrow (H_2)_2 + H_2$, i.e., particularly at the higher densities. The binding energy is usually very small; for the hydrogen complex $(H_2)_2$, it is about 4×10^{-4} eV.[26] Hence, such a complex, once formed, will hardly survive the next collision if kT is much greater than the binding energy, and a destruction reaction, which is the inverse of the above reaction, is important. The equilibrium concentration of these dimers can be derived under the assumption that the only removal rate is the inverse of the above reaction (except for the metastable dimers,[27] which decay possibly on their own). We write after[27] their density n_d

$$n_d = X_2 n, \tag{4}$$

where the mole fraction X_2 is a theoretically known function of the temperature T and proportional to the pressure. n is the neutral density, and n_d is proportional to the square of n. From this we calculate a drift velocity for the mixture of monomers and dimers, replacing the mean free path $1/nq$ in the mobility formula by $1/[(n-2n_d)q + n_d q_d]$, where q_d is the cross section for electron scattering by dimers; hence

$$v_e = (e/m)(nqv)^{-1}[1 + X_2(q_d/q - 2)]^{-1}E. \tag{5}$$

Under the assumption that the mean thermal electron speed v is not much affected by the varying dimer concentration, it can be seen from Eq. (5) that the reciprocal drift velocity has become pressure-dependent (by X_2) in the same way as the experimental data, Eq. (1), if $(q_d/q - 2)$ is positive. Then α is to be compared with $X_2\,(q_d/q - 2)/p$.

The molar fractions can be computed[27] under the assumption of a Lennard-Jones 6-12 potential, with constants from Hirschfelder.[28] We obtain

$$X_2/p = 0.16\times10^{-6}\ \text{Torr}^{-1}\ \text{for}\ H_2\ \text{at}\ 300^\circ\text{K},$$

$$X_2/p = 4.9\times10^{-6}\ \text{Torr}^{-1}\ \text{for}\ H_2\ \text{at}\ 77^\circ\text{K},$$

$$X_2/p = 1.3\times10^{-6}\ \text{Torr}^{-1}\ \text{for}\ N_2\ \text{at}\ 300^\circ\text{K},$$

$$X_2/p = 43.\times10^{-6}\ \text{Torr}^{-1}\ \text{for}\ N_2\ \text{at}\ 77^\circ\text{K}. \qquad (6)$$

Under the assumption that the term $(q_d/q-2)$ is of the order of $+1$, we can compare these numbers with the experimental α values (which were called $\nu_1\tau$ in Fig. 2). For hydrogen at the larger energies, the pressure dependence hereby predicted is too weak by an order of magnitude, and by even two orders of magnitude at the lowest electron energies. Besides, if the 77 and 300°K data are compared near a mean electron energy of 25 meV, a difference of a factor of ~30 is to be expected for α, according to Eq. (6). Experimentally, however, the α values are found to be of the same order of magnitude. Therefore, for hydrogen, dimer formation turns out to be of very little interference for the electron drift motion and can certainly be ignored. For nitrogen, dimer formation could in fact be the determining factor, if the computed X_2 were correct. However, it has been shown recently[29] that in many molecular gases, much lower dimer concentrations were found experimentally than theoretically[27] predicted. For nitrogen, for example, the concentrations at atmospheric pressure and 300°K were found to be smaller than in Eq. (6) by more than two orders of magnitude, presumably because of their inherent instability due to rotational energies. Therefore, dimer formation seems to be unimportant in our context, and it will not be discussed any further here.

OTHER HIGH-DENSITY EFFECTS

For low-energy electrons, another pressure effect is thought to be possible. According to B. Kivel,[30] the polarization interaction forces between electrons and neutrals are effectively screened beyond a certain distance r, which is determined by the gas density. This, in effect, means smaller cross sections at higher densities.[30,31] Hence, the drift motion is expected to be faster at high densities, provided the electron energy is small enough (electron wave number $\geqslant$ reciprocal distance). This is in disagreement with the experimental results, probably because our electron energies are too high for this effect to occur.

Similarly, it has been suggested that with an electron mean free path comparable to the range of the electron-molecule forces, a density independence of v_e could not be expected.[4] (For hydrogen at the highest pressures[4] and lowest energies, the electron mean free path is 60 Å, the mean intermolecular distance 10 Å and the range of the electron-molecule force 2.4 Å). We find it difficult to give a theoretical estimate for this effect. However, it has been shown experimentally that the *ion* drift velocites at these high pressures still agree well with the known low-pressure data.[32] For ions, the range of the forces is even larger and the mean free paths smaller, and yet there is no big change in their drift speed. Therefore, we believe that this effect is probably not very strong even at the highest densities considered here.

CONCLUSION

Several effects of high neutral densities on the drift motion of electrons have been discussed, but could not be used to explain the observed effects in hydrogen, deuterium, and nitrogen, with one exception: If the existence of rotational resonances is assumed, then the experimental data at low electron energies can be interpreted in a semiquantitative way.

One can explain a decreasing effect of the pressure [i.e., a decreasing α or $(\nu\tau)_1$] for increasing electron energies, with cross sections for trapping collisions in the order of 20×10^{-16} cm^2. One can understand a slow decrease of $(\nu\tau)_1$ with increasing mean electron energy eD/μ in hydrogen at 300°K, a faster decrease in nitrogen at 300°K, and a very fast one in nitrogen at 77°K, simply from the reasonably well-known resonance level densities, energetic widths, and lifetimes. Furthermore, one can explain why in hydrogen at 77°K no pressure effect has been found[3,5]: There is simply no resonance state available for energies below 15 meV (see Fig. 2 or Table I). Hence electron trapping is impossible at these low energies (i.e., for E/p below 0.015 V/cm Torr). Deuterium, on the contrary, does have a pressure effect at these energies, which again is easily understood in terms of its reduced rotational constant B, if rotational resonances are assumed to exist. As the mean electron energy is increased to about 18 meV, a density effect can definitely be seen in hydrogen at 77°K. All these facts provide a rather strong support for our assumption of the existence of rotational resonance states, because they link well-known, unpopulated rotational energy levels with electron scattering data, with very large cross sections [$(20-30)\times10^{-16}$ cm^2] and detectable lifetimes of the compound state.

Admittedly, the weakness in all these discussions is some remaining ambiguity about possible other interpretations of the observed pressure effect,[3-5] which might have been overlooked in this work. However, the hypothesis of rotational resonances for electrons yields a surprising understanding of many details of these drift data, whereas all the other effects we know of provide partial and unsatisfactory explanations or none at all. We thus feel that, in this paper, arguments in favour of their existence have been raised, in spite of the remaining uncertainties. It is not surprising that these postulated resonances have not yet been found with conventional techniques (i.e., in beam experiments), because of their extremely low energy levels.

At the higher electron energies (near 1 eV) the known single-particle resonances of N_2 and H_2 (which occur near 2.3 eV and are known to be wide) may be expected to produce a pressure dependence of the electron drift motion in these gases of the observed order of magnitude.

ACKNOWLEDGMENT

It is a pleasure to acknowledge valuable communication with a great number of colleagues, particularly with Dr. J. C. Browne, Dr. R. W. Crompton, Dr. B. K. Gupta, Dr. N. F. Lane, Dr. J. J. Lowke, Dr. A. V. Phelps, and Dr. H. S. Taylor.

APPENDIX

As noted above,[22] Eq. (2) is valid only in the case that no more than one electron trapping state needs to be considered. With several trapped-electron states active simultaneously, a somewhat more complicated system of equations is to be used for the derivation of the apparent drift velocity v_e, which is a function of $\nu_1, \nu_2, \cdots$ and $\tau_1, \tau_2, \cdots$, the individual resonance scattering frequencies and lifetimes of the trapped electrons. This set can be written

$$\frac{\partial n_e}{\partial t}+v_{e0}\frac{\partial n_e}{\partial x}=-(\nu_1+\nu_2+\cdots)n_e$$

$$+\left(\frac{1}{\tau_1}n_1+\frac{1}{\tau_2}n_2+\cdots\right)\frac{\partial n_j}{\partial t}=\nu_j n_e-\frac{1}{\tau_j}n_j \qquad (7)$$

$$(j=1,2,\ldots),$$

where n_e and n_j $(j=1,2,\cdots)$ designate the free and trapped electron densities, respectively. Now we define the total numbers of the free and trapped electrons

$$i=\int n_e dx \text{ and } k_j=\int n_j dx \quad (j=1,2,\cdots) \qquad (8)$$

and their centers of mass

$$\bar{x}=\int x n_e dx/i;\quad \bar{x}_j=\int x n_j dx/k_j. \qquad (9)$$

By integrating the Eqs. 7 with respect to dx and with respect to xdx, a relationship for v_e and v_{e0} is obtained.

$$di/dt=-(\nu_1+\nu_2+\cdots)i+[\tau_1^{-1}k_1+\tau_2^{-1}k_2+\cdots] \qquad (10)$$

$$dk_j/dt=\nu_j n_e-\tau_j^{-1}k_j \quad (j=1,2,\cdots) \qquad (11)$$

$$d(\bar{x}i)/dt-v_{e0}i=-(\nu_1+\nu_2+\cdots)\bar{x}i+[\tau_1^{-1}\bar{x}_1k_1+\tau_2^{-1}\bar{x}_2k_2+\cdots] \qquad (12)$$

$$d(\bar{x}_jk_j)/dt=\nu_j\bar{x}_j-\tau_j^{-1}\bar{x}_jk_j. \qquad (13)$$

Here it has been assumed that the function n_e of x is constricted to a certain area near $\bar{x}$ and $n_e \rightarrow 0$ as $x \rightarrow \pm\infty$. In other words, it is assumed that there is but one "cloud" of electrons near $\bar{x}$ and no electrons elsewhere. For equilibrium, the time derivatives of i and k_j become zero, and the apparent drift velocity v_e is given by $v_e=d\bar{x}/dt$. Hence Eq. (12) reads

$$(v_{e0}-v_e)i=\sum_j(\nu_j\bar{x}i-\tau_j^{-1}\bar{x}_jk_j), \qquad (14)$$

where the terms in parentheses on the right-hand side will be replaced by $k_jd\bar{x}/dt$, according to Eq. (13), and the k_j by $k_j=\nu_j\tau_j i$, from Eq. (11). Hence we obtain

$$(v_{e0}-v_e)i=\sum_j\nu_j\tau_j i d\bar{x}_j/dt, \qquad (15)$$

and the free-electron number i cancels out. Finally we replace the time derivatives of $\bar{x}_j$ by v_e, since the centers of mass of all the trapped electron states obviously "move" with the same speed as the free electron swarm, because of the equilibrium condition. (The free and trapped electrons drift as one package). After rewriting Eq. (15), we obtain

$$v_e=v_{e0}/(1+\sum_j\nu_j\tau_j), \qquad (16)$$

which is a more general form than Eq. (2) and reduces to it for but one trapping state. It still has formally the same pressure dependence as Eq. (2), because all the ν_j's are proportional to the pressure, and the τ_j's do not depend upon the pressure (provided a limiting pressure is not exceeded). The average of $(\nu\tau)$ is equal to

$$\langle\nu\tau\rangle_{\text{av}}=\sum_j\nu_j\tau_j \qquad (17)$$

and proportional to the pressure.

---

*This work was supported by the Joint Services Electronics Program, Research Grant AF-AFOSAR-766-67.

[1] L. B. Loeb, Basic Processes of Gaseous Electronics (University of California Press, Berkeley, 1960).

[2] W. P. Allis, in Handbuch der Physik, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 21, p. 383.

[3] J. J. Lowke, Australian J. Phys. 16, 115 (1963).

[4] R. Grünberg, Z. Physik 204, 12 (1967).

[5] R. W. Crompton, M. T. Elford, and A. I. McIntosh, Australian J. Phys. 21, 43 (1968).

[6] L. S. Frost and A. V. Phelps, Phys. Rev. 127, 1621 (1962).

[7] J. Vogel, Z. Physik 148, 355 (1957).

[8] L. Frommhold, Fortschr. Physik 12, 597 (1964).

[9] G. S. Hurst, L. B. O'Kelly and J. A. Stockdale, Nature 195, 66 (1962); J. Chem. Phys. 38, 2572 (1963).

[10] J. L. Pack, A. V. Phelps, J. Chem. Phys. 44, 1870 (1966).

[11] L. B. Loeb, Phys. Rev. 48, 684 (1935).

[12] R. Haas, Z. Physik 148, 177 (1957).

[13] G. J. Schulz, Phys. Rev. 116, 1141 (1959); 125, 229 (1962); 135, A988 (1964).

[14] H. S. Taylor, G. V. Nazaroff, and A. Golebiewski, J. Chem. Phys. 45, 2872 (1966).

[15] I. Eliezier, H. S. Taylor, and J. K. Williams, J. Chem. Phys. 47, 2165 (1967).

[16] R. H. Ritchie and J. E. Turner, Z. Physik 200, 259 (1967).

[17] L. M. Chanin, A. V. Phelps, and M. A. Biondi, Phys. Rev. 128, 219 (1962).

[18] Although the lifetimes of the known molecular resonance states are very short, it can be said that they are definitely longer than the duration of an ordinary elastic scattering collision of an electron and a molecule, which is in the order of 10^{-15} sec for thermal electrons. Hence it is not absurd to talk of electron trapping in connection with resonance scattering.

[19] The lifetime of this state is an estimated 10^{-14} sec; see Ref. 15. Hence an assumed mean cross section of 3×10^{-17} cm^2 for this state at $\bar{\epsilon} = 1$ eV would yield $(\nu\tau)_1 = 0.6 \times 10^{-6}$ Torr^{-1}, in agreement with the experiment.

[20] D. J. Kouri, J. Chem. Phys. 45, 154 (1966).

[21] G. Herzberg, Spectra of Diatomic Molecules (D. van Nostrand Co., Inc., Princeton, 1950).

[22] A rigorous derivation requires one continuity equation for the free electrons, and one for each trapping state, with different lifetimes τ_1, τ_2, ..., etc. (see the appendix).

[23] D. E. Golden, Phys. Rev. Letters 17, 847 (1966).

[24] A. Watanabe and H. L. Welsh, Phys. Rev. Letters 13, 810 (1964).

[25] N. Bernardes and H. Primakoff, J. Chem. Phys. 30, 691 (1959).

[26] R. G. Gordon and J. K. Cashion, J. Chem. Phys. 44, 1190 (1966).

[27] D. E. Stogryn and J. O. Hirschfelder, J. Chem. Phys. 31, 1531 (1959); 33, 942 (1960).

[28] Joseph Hirschfelder, Charles Curtiss, and R. Bird, Molecular Theory of Gases and Liquids (John Wiley & Sons, Inc., New York, 1954) and Natl. Bur. Std. (U. S.), Circ. No. 564 (1955).

[29] T. A. Milne and F. T. Greene, J. Chem. Phys. 47, 3668 (1967).

[30] B. Kivel, Phys. Rev. 116, 926 (1959).

[31] T. F. O'Malley, Phys. Rev. 130, 1020 (1963).

[32] E. K. Müller, Z. Angew. Physik 21, 475 (1966).

Dissociative Attachment in CO and NO[†]

P. J. Chantry
Westinghouse Research Laboratories, Pittsburgh, Pennsylvania 15235

(Received 18 March 1968)

The electron energy dependences of the cross sections and of the ion kinetic energy distributions have been measured for O$^-$ production from CO and NO. The present apparatus permits total collection measurements as well as kinetic energy analysis and mass identification of the ions produced. It is shown that in CO two reactions contribute to the single peak in the cross section, whereby carbon atoms are produced in their ground state and in their first excited state (^1D) respectively. The first reaction is predominant, and known from previous work to have a peak cross section of 2.0×10^{-19} cm^2. Normalized to this, the second reaction is shown to have a peak cross section of 9.5×10^{-21} cm^2. In NO it is shown that O$^-$ production proceeds exclusively through the reaction $e + \mathrm{NO} \to \mathrm{O}^- + \mathrm{N}^*$ where N* is the first excited state (^2D). No O$^-$ ions are observed corresponding to the formation of ground state N. Nor is there any evidence for the production of the second excited state of nitrogen, N(^2P), postulated by Dorman to account for the structure in the attachment cross section.

INTRODUCTION

In two previous publications,[1,2] Chantry and Schulz have discussed in some detail the problems attending the experimental determination of the energetics of dissociative attachment reactions using electron beams, and the extent to which these problems are alleviated by making suitable direct observations of the ion kinetic-energy distributions as a function of electron energy. The superiority of such a technique over earlier techniques involving retarding potential analysis of the ion energies was demonstrated in Ref. 2 (hereafter referred to as CS) in a study of O$^-$ production from O$_2$. The purpose of the present paper is to report the results of similar measurements on the reactions

$$e + \mathrm{CO} \to \mathrm{O}^- + \mathrm{C}, \tag{1}$$

and

$$e + \mathrm{NO} \to \mathrm{O}^- + \mathrm{N}. \tag{2}$$

These reactions were first observed by Vaughan[3] and by Tate and Smith[4] and have been studied repeatedly[5] since that time. The present study of the reaction (1) was undertaken to establish that the threshold does indeed correspond to the accepted values of the dissociation energy D and of the electron affinity A. In such cases as this, where the cross section rises very sharply, probably vertically, to a maximum value at threshold, the determination of the true threshold from a measurement of the energy dependence of the cross section presents an unfolding problem which requires a detailed knowledge of the electron energy distribution used.[6] An alternative approach is to measure the most probable ion energy as a function of most probable electron energy over as wide a range as possible, and extrapolate the data in the theoretically expected linear manner to the threshold. This method, used in CS to study