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Townsend Ionization Coefficient for Hydrogen and Deuterium

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The Townsend ionization coefficient α/p_0 (cm×mm Hg at 0°C)$^{-1}$ for hydrogen and deuterium has been measured as a function of E/p_0 (volts/cm×mm Hg at 0°C) over an extended range. The results for H_2 have been compared critically with those of previous workers. They agree well with several recent redeterminations over limited ranges of E/p_0, but not with several earlier extensive investigations. The composite results for H_2 ($15<E/p_0<1000$), and present data for D_2 ($18<E/p_0<600$), are presented in graphical and tabular form. The difference between the two coefficients is discussed in terms of the molecular properties of the two gases. It appears that the difference in energy loss by recoil on electron impact is insufficient to explain the observed effect.

I. INTRODUCTION

THE first extensive measurements of the Townsend ionization coefficient for hydrogen as a function of E/p (ratio of electric field to gas pressure) were reported in 1923 by Ayres.[1] A redetermination in 1938 by Hale[2] gave considerably different results. Several more recent determinations[3-7] over limited ranges of E/p have indicated that both determinations were at least partly in error. The experiment has therefore been repeated over a wide range of the experimental variable E/p; this paper presents the results of these measurements. In addition, a detailed comparison is made with other recent experimental data. In this manner, a consistent tabulation of the ionization coefficient over the widest possible range of E/p is obtained.

A simple theoretical argument, to be given later, shows that the ionization coefficients for deuterium and hydrogen should be identical at very high values of E/p; and the coefficient should be higher for deuterium at low values of E/p. The experiment has been repeated in the same apparatus for deuterium, and a comparison is made with hydrogen.

The ionization coefficient is defined in the following manner. Consider a pair of infinite parallel planes, a distance d apart, with a voltage V and field $E=V/d$ applied between them, and a pressure p_0 (reduced to 0°C) of gas contained therein. An electron current i_0 leaving the cathode by photoemission will ionize gas molecules, producing an electron avalanche traveling toward the anode and an ion current toward the cathode. The total current between the plates is[8]

$$i=\frac{i_0 e^{\eta(V-V_0)}}{1-\gamma(e^{\eta(V-V_0)}-1)}. \tag{1}$$

The quantity η is the ionization rate measured in units of reciprocal volts, and is a function of E/p_0 only. It is the quantity α/E, where α is the first Townsend coefficient. The constant V_0 allows in an approximate manner for the fact that all the electrons near the cathode have low energy, and must fall through a certain potential (V_0) before a terminal velocity distribution is established. The exponent in (1) may also be written in the completely equivalent form $\exp(\alpha/p_0)p_0(d-x_0)$, where now $\alpha/p_0=\eta E/p_0$ (cm×mm Hg)$^{-1}$ represents the ionization coefficient. Either form will be used as convenience dictates.

The coefficient of secondary electron emission by

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[1] T. L. R. Ayres, Phil. Mag. **45**, 353 (1923).

[2] D. H. Hale, Phys. Rev. **55**, 815 (1939); see also L. B. Loeb, *Basic Processes of Gaseous Electronics* (University of California Press, Berkeley, 1955), p. 691.

[3] W. Fucks and F. Kettel, Z. Physik **116**, 657 (1940).

[4] L. J. Varnerin and S. C. Brown, Phys. Rev. **79**, 946 (1950).

[5] Wilkes, Hopwood, and Peacock, Nature **176**, 837 (1955); Proc. Roy. Soc. (London) (to be published).

[6] Crompton, Dutton, and Haydon, Nature **176**, 1079 (1955); Proc. Phys. Soc. (London) **B69**, 1 (1956).

[7] Rose, DeBitetto, and Fisher, Nature **177**, 945 (1956).

[8] See, for example, J. M. Meek and J. D. Craggs, *Electrical Breakdown of Gases* (Clarendon Press, Oxford, 1953), p. 68.

positive ions is γ; as the voltage is raised, the γ term in the denominator of Eq. (1) eventually reaches unity, and the gas breaks down. At voltages considerably below breakdown, however, the γ term is unimportant and may be neglected. In this range, therefore, if the plate separation d and voltage V are increased proportionately, thus keeping E/p_0 constant, the current i increases exponentially with V. In practice, the experiment is performed in just that way.

II. EXPERIMENTAL TECHNIQUE

Figure 1 shows a simplified diagram of the parallel plate tube and electrical connections. Ultraviolet light shines from below through a quartz window and through the perforated anode onto the movable molybdenum cathode, 5 cm in diameter. The cathode can be moved vertically and is restrained laterally by Kovar guides running in shrunk glass tubing. The plate separation can be adjusted to preset positions in the range 0–1 cm by the notched shaft and fixed catch. Not shown are the pump lead, an iron slug sealed in glass and fixed to the top of the shaft, by which the cathode is raised magnetically; and two aluminum shields evaporated onto the inside of the glass envelope, at cathode and anode potentials, respectively. The plate separation is adjustable in steps of about 0.064 cm, and determinable to about 0.001 cm. The tube is connected to a vacuum apparatus, and can be sealed off from the pumps by a mercury cutoff. Gas can be admitted through an all-metal diaphragm-type valve. In these experiments, hydrogen was obtained either from one liter reagent grade flasks, or from the decomposition of uranium hydride. In this latter connection, reactor grade uranium chips were degassed in a quartz tube at about 800°C in vacuum, and were allowed to combine with reagent grade gas at about 200°C. The hydride could then be pumped at room temperature, and subsequently decomposed at temperatures $\sim$300°C. It may be remarked here that both sources of hydrogen gave the same experimental results. Deuterium was similarly obtained from uranium deuteride. Gas pressure in the experimental tube is measured with an accuracy of ± 1 percent by McLeod gauges.

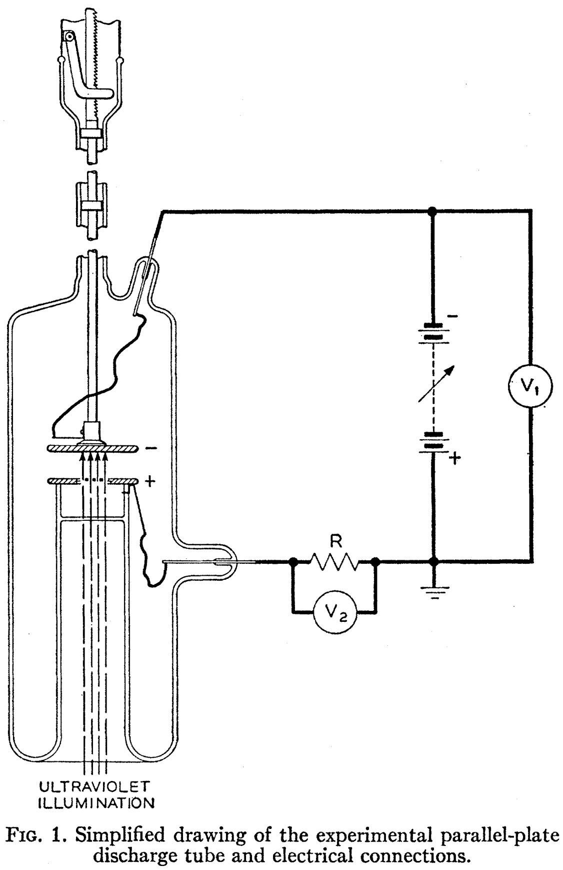

FIG. 1. Simplified drawing of the experimental parallel-plate discharge tube and electrical connections.

The voltage across the plates is given by $V_1 - V_2$ (Fig. 1). V_1 is a 0–2000 volt battery supply; by means of a divider network, it is compared with a standard cell at each reading. The resistor R is adjustable in steps from 10^7–10^{12} ohms; the voltage V_2 (0–2 v) across it is read by an electrometer, and is a measure of the current.

The degassing procedure prior to each run was as follows. The experimental tube was baked at 300°C, and the auxiliary equipment at about 400°C; prior to the formation of the UH_3 or UD_3 (which have dissociation pressures $\sim 10^{-6}$ mm Hg at room temperature) the pressure was 10^{-9} mm Hg or lower. In addition, just before the run, the cathode surface was bombarded by a high current pulsed discharge in the purified gas. During bombardment, the average cathode temperature reached about 850°C, and the surface temperature during a pulse was estimated to be $\sim$1500°C. This spent gas was then pumped out, and the data were obtained after admitting fresh gas. On several occasions, the operation of baking and bombarding was performed twice in succession. The experimental results were not altered by the second operation. It was not possible to heat the cathode *in vacuo* by rf induction.

A mass analysis was made of the deuterium used in the experiment, the original purpose being to check the percentage of normal H_2. Besides 0.5% H_2 (which will have negligible effect on the experimental results), it was surprising to discover 0.04% CO and a trace of D_2O. The sample bottle itself appears most likely to be the source of contamination. In particular, it is inconceivable that even $10^{-4}\%$ of any impurity could arise either from the vacuum system (5.5×10^{-10} mm Hg background pressure) or uranium (7.5×10^{-9} mm Hg at 385°C). If CO, CO_2, O_2, N_2, or D_2O had been initially present in the deuterium flasks, the gases should all be converted to oxides or nitrides of uranium. The difference in free energy is very large; in particular, it is almost 200 kilocalories/mole for the reaction

$$2CO + U \rightarrow UO_2 + 2C.$$

In addition, all uncombined gases ($\approx 10^{-3}\%$ of the original volume) are removed by pumping on the UD_3. Thus CO cannot be retained in the system as such. Turning now to the sample bottle, one finds that there were about 4×10^{16} CO molecules in it. This corresponds to about one monolayer over its inside surface, or the equivalent of 10–20 monolayers released from the interior of the glass constriction which was heated to the melting point. There is considerable independent evidence that this amount of CO_2 (which would be reduced to CO by the deuterium) can well be evolved in such a seal-off technique.

Data were obtained at various pressures p_0 of H_2 or D_2 in the range $0.5<p_0<45$ mm Hg. Four typical runs in H_2 at pressures between 2.7 and 10.5 mm Hg are shown in Fig. 2. Here, the tube current V_2/R is plotted in arbitrary units *vs* tube voltage V_1-V_2; the plate separation is adjusted to keep E constant.

III. IONIZATION COEFFICIENT FOR HYDROGEN

The results will now be presented, and critical comparison made with other data, all of which have been reduced to 0°C. The first comparison is with the early extensive determinations of Ayres and Hale; for this purpose, it is convenient to express them in terms of the coefficient η. Figure 3 shows these data; the present results are shown by the circles and solid line drawn through them. Except near the extremes of E/p_0, the results should be accurate within $\pm 2\%$. Accuracy at both extremes cannot be stated categorically from a study of this experiment alone. It will be discussed below when comparison is made with other experiments. No comprehensive data were obtained for the coefficient V_0 of Eq. (1); however, study of the $\ln i$ *vs* V characteristics at low voltage (0–50 volts) indicates that in the range $40<E/p_0<300$, V_0 is about 20 volts.

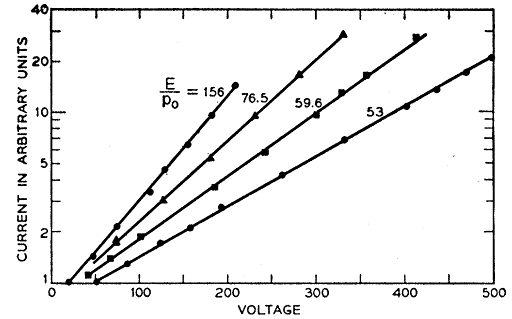

FIG. 2. Four typical sets of data of tube current *vs* applied voltage at constant E/p_0, for H_2.

The dashed curve of Fig. 3 attributed to Ayres[1] has been prepared from his table of α/p *vs* E/p. Ayres shows little actual data; his table was itself prepared from a smoothed curve. No reference temperature is stated, and 18°C is assumed. One notes fairly good agreement between Ayres' results and the present ones, except for $E/p_0<35$. This sort of error is just what would be expected if Ayres' gas were not sufficiently pure, as can be seen by the following calculation. At intermediate or low E/p the number of collisions made by an electron in crossing the gap of d cm is approximately $1.5\times 10^4(p_0d)/(E/p_0)$. At low E/p, pd must be large if appreciable ionization is to be obtained; in the present experiment, for example, $pd\approx 45$ cm×mm Hg at $E/p_0\approx 20$. Thus, if an impurity with low ionization potential is present in small amount, the chance of its ionization in preference to hydrogen is much greater at low than at high E/p. Inasmuch as most impurities (O_2, H_2O, N_2, Hg) have lower ionization potential than H_2, it appears reasonable that Ayres' results might be affected in just this way.

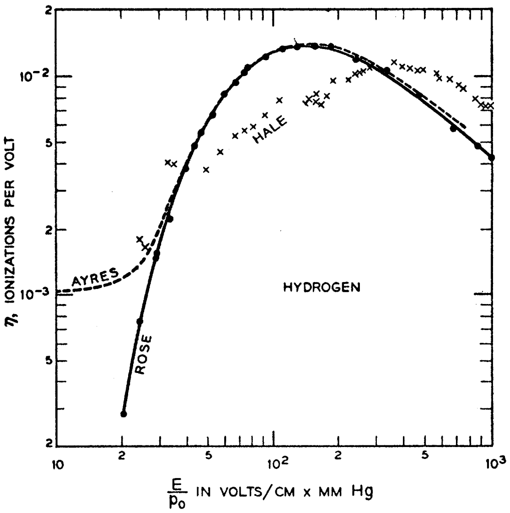

FIG. 3. The ionization coefficient η volts^{-1} for H_2 plotted *vs* E/p_0 volts/cm×mm Hg, at 0°C. The circles and solid curve are the present results. The dashed curve and crosses represent the earlier results of Ayres and Hale, respectively.

Referring again to Fig. 3, the crosses are calculated from Hale's data of α/p *vs* E/p listed by Loeb,[2] and reduced from 20°C to 0°C. It is difficult to point out just how the discrepancy between Hale's data and the other sets arises. Hale himself noted this discrepancy with Ayres, and postulated that Ayres' results were due to improper liquid air trapping of the vacuum system. Hale observed that if he used a standard re-entrant trap and admitted hydrogen rapidly to the system, he obtained Ayres' results. If he admitted the gas slowly, and in particular used a spiral trap made of small diameter tubing, he obtained his published data. Such a trap is, of course, much better for removing mercury and water vapor, but it cuts the pump speed to the experimental tube drastically. In order to check this very point, the present experiments were done both with and without a spiral trap in addition to the normal one. No difference was found, except that the experimental tube took a good deal longer to clean up.

The indirect experimental measurements of Varnerin

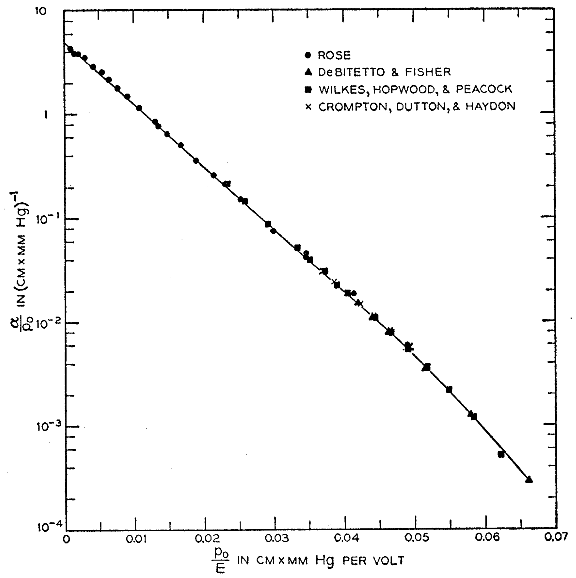

FIG. 4. The ionization coefficient α/p_0 (cm×mm Hg)$^{-1}$ at 0°C *vs* p_0/E cm×mm Hg/volt at 0°C for H_2, showing the results of several workers.

and Brown[4] (not shown here) do not agree well with the present data. Their results are higher by a factor of three near $E/p=20$, and lower by a factor of 1.5 near $E/p=100$. Their theory, however, gives fair agreement ($\pm 15\%$) with our experimental results in the range $40<E/p_0<100$. The data of Fucks and Kettel[3] (not shown) are somewhat suspect, in that they do not show α/p_0 as a single valued function of E/p_0 above $E/p\approx 40$. Below this value, their data lie about 10% above the present results.

The Paschen minimum in H_2, i.e., minimum of breakdown voltage *vs* the product of pressure and gap spacing, will occur at $\eta_{\max}$, which is at $E/p_0\approx 140$. The value of η at appreciably higher E/p is therefore less important from an experimental point of view. In principle, its value tends to lose meaning, as the average electron energy at high E/p is not a function of E/p alone, but also of the voltage. If this effect is large, one should expect the $\ln i$ *vs* V plots of Fig. 2 to be curved upward over their entire range. The fact that they were straight over ranges of i/i_0 from 1 to 20 appears to indicate that the effect is not overwhelming, and that an effective value of η can be defined for such circumstances. It may also be noted that Johnson's[9] values of α'/p_0, determined indirectly in a coaxial geometry, agree rather well (0–10% lower) with the present results for $E/p_0<100$. Above this, Johnson's results are higher, being about 50% higher near $E/p=500$.

The regime at low E/p is particularly important from an experimental point of view. Recent measurements of α/p in this range have been made by Wilkes, Hopwood, and Peacock[5] (reference temperature 20°C); Crompton, Dutton, and Haydon[6] (20°C); and DeBitetto and Fisher (0°C). In order to examine this low E/p region most critically, it is convenient to plot α/p_0 *vs* p_0/E. All pertinent data, corrected to 0°C, are shown in this way in Fig. 4. One notes that for $p_0/E<0.059$ ($E/p_0>17$) the agreement is excellent: about 65% of the points lie within 2% of the curve. The three values of α/p_0 obtained by Geballe and Harrison[10] also lie close to the curve. The general agreement is especially gratifying when one considers that the pressure varied over the range $0.5<p<700$ mm Hg in the various investigations. From the general nature of the results, then, one may conclude that α/p_0 has been determined over the range $E/p_0>17$ with an accuracy of about 2%. In the range $15<E/p_0<17$, the lack of independent check makes the value less certain. It is worth noting that over the range $0<p_0/E<0.045$, i.e., $E/p_0>22$, $\ln\alpha/p_0$ *vs* p_0/E is a straight line $\pm 2\%$; in this range

$$\alpha/p_0=5.1\exp[(-138.8\pm 0.4)p_0/E]. \tag{2}$$

Several approximate theories[11] have been put forward which predict such a form, but none should be that accurate over such a range. No particular significance is therefore attached to this exact dependence at the present time. Table I lists values of α/p_0 *vs* E/p_0 taken from the smoothed curve of Fig. 4.

TABLE I. Ionization coefficient α/p_0 (cm×mm Hg)$^{-1}$ at 0°C *vs* E/p_0 (volts/cm×mm Hg) at 0°C for hydrogen and deuterium.

E/p_0	α/p_0 hydrogen	α/p_0 deuterium
15	2.6×10^{-4}	
16	5.7×10^{-4}	
17	1.06×10^{-3}	
18	1.91×10^{-3}	4.3×10^{-3}
20	4.60×10^{-3}	1.00×10^{-2}
22	9.2×10^{-3}	1.88×10^{-2}
24	1.56×10^{-2}	3.0×10^{-2}
26	2.42×10^{-2}	4.4×10^{-2}
28	3.58×10^{-2}	6.0×10^{-2}
30	4.95×10^{-2}	7.6×10^{-2}
35	9.6×10^{-2}	1.28×10^{-1}
40	1.56×10^{-1}	1.96×10^{-1}
45	2.32×10^{-1}	2.8×10^{-1}
50	3.15×10^{-1}	3.7×10^{-1}
60	5.00×10^{-1}	5.7×10^{-1}
70	6.9×10^{-1}	7.7×10^{-1}
80	8.9×10^{-1}	9.6×10^{-1}
90	1.08	1.16
100	1.26	1.34
125	1.67	1.72
150	2.02	2.1
175	2.32	2.37
200	2.55	2.6
250	2.95	3.0
300	3.21	3.25
400	3.60	3.6
500	3.90	3.9
600	4.10	4.1
800	4.3	
1000	4.45	

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[9] G. W. Johnson, Phys. Rev. 73, 284 (1948).

[10] L. B. Loeb, reference 2, p. 414.

[11] See, for example, Emeléus, Lunt, and Meek, Proc. Roy. Soc. (London) A156, 394 (1936).

IV. IONIZATION COEFFICIENT FOR DEUTERIUM

Figure 5 shows α/p_0 *vs* p_0/E for deuterium, with the smoothed curve for hydrogen also shown for comparison. The semilogarithmic plot is not straight for deuterium. However, a relation $\alpha/p_0=5.1\exp(-124.8p_0/E)$ fits the smoothed curve at $p_0/E=0$, 0.034, and 0.050, and is within 10% elsewhere. The accuracy does not appear to be quite as good as that for hydrogen, but should be ±5% or better. Table I shows values of α/p_0 *vs* E/p_0, taken from the smoothed curve.

V. COMPARISON OF RESULTS IN HYDROGEN AND DEUTERIUM

Note that at $p_0/E\rightarrow 0$, α/p_0 is the same for H_2 and D_2, while at high p_0/E, the data for D_2 lie higher by about a factor of 2. A simple argument shows that a trend in this direction is to be expected. The electronic excitation and ionization probabilities of H_2 and D_2 are virtually identical. At low p_0/E, the average electron energy is high, and electron energy losses are principally to excitation and ionization. One should therefore expect to find the same ionization coefficients, as is the case. At high p_0/E, average electron energy is low, and an electron loses considerable energy through the immense number of so-called "elastic" impacts with neutral molecules. These collisions are not quite elastic, however; conservation of momentum of the electron-molecule system requires an average $2m/M$ fractional loss of the electron energy per collision, where m/M is the mass ratio. The loss is therefore lower in D_2 (1/3674) than in H_2 (1/1837). Thus, at the same value of p_0/E, more energy is available for ionization in D_2, and α/p_0 should be higher.

Preliminary calculations indicate that this effect is several times too small to explain the observed difference, at least in the range $0.01<p_0/E<0.025$. A theoretical calculation of α/p_0, based on the Boltzmann transport equation, is in progress, and shows that in that range, the two gases should behave almost identically. The only other differences between the two gases are the effect of the width of the Franck-Condon region on the sharpness of the various excitation potentials, and the rotational and vibrational excitations.

The first of these effects appears to be small; for a harmonic oscillator, the width of the region in the ground state varies as $M^{-\frac{1}{4}}$. The principal effect here will arise in transitions induced by electron impact from the ground state to the repulsive $1^3\Sigma_\mu$ state, whose energy is a strong function of internuclear separation. For H_2, the minimum energy is about 8.8 ev, and for D_2 it should be no more than 0.3 ev higher. In addition, violations of the Franck-Condon principle are easier for the case of H_2. These effects are in the direction of giving more electron loss by excitations in H_2, and hence of explaining the difference in the curves of Fig. 5; but they appear hardly sufficient.

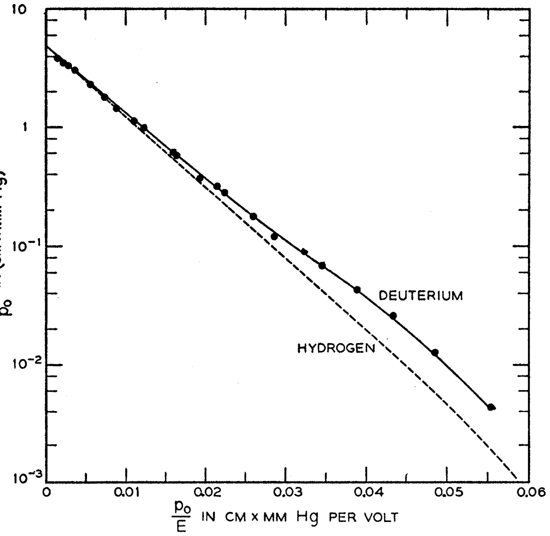

FIG. 5. The ionization coefficient α/p_0 (cm×mm Hg)$^{-1}$ at 0°C *vs* p_0/E cm×mm Hg/volt at 0°C for D_2. The results for H_2 are also shown for comparison.

The lower lying rotational excitations probably do not play an important role, at least in comparison with the vibrations, because their energy is so much smaller. The vibrational excitations may be a reasonably efficient energy loss mechanism. The states are closer together for D_2 than for H_2 (0.36 *vs* 0.51 ev), and one might at first conclude that excitation is more likely in D_2, which is in the wrong direction to explain the difference in the curves. But also to be considered are the forms of the excitation probabilities to the various vibrational states as functions of electron energy, and the actual distribution of electron energies in the gas. The most probable energy is several electron volts, so that there are less electrons near 0.36 than at 0.51 ev. In view of these theoretical involvements, it is impossible at present to explain properly the difference in the ionization curves. A general theoretical study of the problem is being continued.

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