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# Mobility of Mercury Ions in Mercury Vapor*

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Measurements of mercury ion drift velocities and mobilities in mercury vapor by the Hornbeck technique have been made over a range of electric-field strength divided by reduced pressure ($E/p_0$) from 40 to 1500 V/(cm×mm Hg). Two stable mercury ions, believed to be $Hg^+$ and $Hg_2^+$, have been observed. The zero-field mobility of the two ions found by a long extrapolation gives the atomic ion $Hg^+$ a zero-field mobility of $0.24\pm0.03$ cm$^2$/V-sec while the molecular ion mobility is estimated at $0.45\pm0.05$ cm$^2$/V-sec. The atomic ion value is in good agreement with theory; the molecular ion value is appreciably lower than the theoretical prediction. Charge exchange cross sections for $Hg^+$ in Hg computed from present data are higher by a factor of nearly 1.5 than values measured directly but are qualitatively in line with rare-gas values measured by the present method. The secondary electron emission coefficient from a surface due to positive ion bombardment $\gamma_i$ has been calculated for the two cathodes used: $\gamma_i$ for molybdenum is estimated by $5\times10^{-5}$ electron per positive ion striking the cathode surface; $\gamma_i$ for an oxide-coated nickel surface is estimated at $2\times10^{-2}$ electron per positive ion striking the cathode.

## I. INTRODUCTION

THE mobility of ions in gases has been measured for a great many combinations of ions and gases but not directly for mercury ions in mercury vapor. Such a measurement would seem of considerable interest because mercury vapor is one of the few monatomic gases which is not a rare gas and at the same time is easily available. Moreover, there is only limited evidence available concerning the presence or absence of $Hg_2^+$ ions in mercury discharges. The evidence for existence of $Hg_2^+$ is due to Arnot and Milligan[1] who, in 1935, succeeded in showing that both $Hg^+$ and $Hg_2^+$ could be identified by mass spectroscopy and that the molecular ion had a binding energy of 0.9 eV.

## II. EXPERIMENTAL PROCEDURE

A device classifiable as a Hornbeck pulsed-Townsend discharge tube[2] was accordingly assembled to measure the mobility of mercury ions in mercury vapor. This device has been used by other experimenters with minor modifications.[3–5] Since the method has been extensively described in this journal, no details are given except for the new features peculiar to mercury vapor problems. The usual high-vacuum techniques were employed, a vacuum of $10^{-8}$ mm Hg being attained before any readings were taken.

A small reservoir in the main experimental tube was filled by running mercury up a barometric column into the bottom of the tube. The column was then partially lowered to minimize heat conduction and cooling in the reservoir. The column also served to close a cutoff sealing the tube from the pumping system.

The mercury vapor pressure was controlled by temperature. The entire tube, including the reservoir and the cutoff, were within an oven within which it was possible to sustain a reasonably uniform temperature. Thermocouples were attached at five different points on the Pyrex tube walls. A spread of 3°C among the readings was almost inevitable but introduced no greater error than other factors causing dispersion among the velocity readings. Saturated mercury vapor was then presumed to fill the tube, in equilibrium with the lowest temperature reading. The saturation pressures were taken from the Handbook of Chemistry and Physics.[6]

Both the ionic mobility and the related variable $E/p_0$, the field strength-to-pressure ratio, require the use of a reduced pressure, $p_0$, the pressure at 0°C which would give the same density as is actually in the tube at the temperature $T$. Thus, a conversion $p_0 = p\ 273°\mathrm{K}/T$ was always introduced, where $T$ is the tube temperature in °K and $p$ is the saturated vapor pressure obtained from the Handbook.

Following a procedure commonly used in the Hornbeck method, two different cathodes were employed, one of pure molybdenum, the other of nickel coated with a $BaCO_3$, $SrC_2O_4$ mixture reduced to BaO and SrO. The coated cathode, with an appreciably lower work function, made drift velocity readings possible at lower values of $E/p_0$ than the molybdenum cathode allowed. The difference is largely a matter of a higher yield of electrons producing enough ions to permit a measurement at lower values of $E/p_0$.

## III. EXPERIMENTAL RESULTS

### A. Mobility

As in the rare gases, two distinct ionic speeds could be identified at some values of $E/p_0$ (see Fig. 1), and

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[1] F. L. Arnot and J. C. Milligan, Proc. Roy. Soc. (London) **A153**, 359 (1935).

[2] J. A. Hornbeck, Phys. Rev. **83**, 374 (1951); **84**, 615 (1951).

[3] R. N. Varney, Phys. Rev. **88**, 362 (1952); **89**, 708 (1953); **93**, 1156 (1954).

[4] E. C. Beaty, Phys. Rev. **104**, 17 (1956).

[5] F. R. Kovar, E. C. Beaty, and R. N. Varney, Phys. Rev. **107**, 1490 (1957).

[6] *Handbook of Chemistry and Physics* (Chemical Rubber Publishing Company, Cleveland, Ohio, 1963).

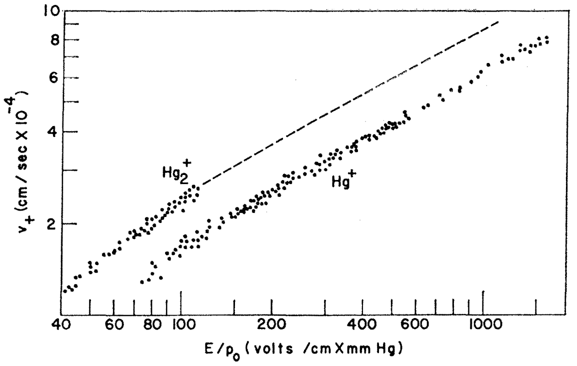

FIG. 1. Log-log plot of drift velocity of mercury ions in mercury vapor versus $E/p_0$. The dashed line is an extrapolation of the $Hg_2^+$ data with a slope of $\frac{1}{2}$ to higher $E/p_0$ values.

the usual interpretation is advanced that the two speeds should be associated with two different types of ions. Since Arnot and Milligan[1] clearly identified $Hg^+$ and $Hg_2^+$, such an identification is at once suggested here. Parallelism with the rare gases, all of which show atomic and diatomic ions, further supports the identification. The disappearance of the faster ion with increasing $E/p_0$ corresponds with Arnot and Milligan's observation that $Hg_2^+$ disappeared at lower values of $p$ and suggests that the faster ion in the present work is $Hg_2^+$. It may be noted that if the fast ion were, for example, $Hg^{++}$, it should thrive with lower $p$ and higher $E$ whereas, in the present experiment, the fast ion disappears under these circumstances. The diatomic rare-gas ions all have greater drift velocities than their corresponding monatomic ions at the same $E/p_0$. The thought that the heavier molecular ion should be slower is outweighed by the fact that atomic ions moving in their parent atomic gas all have large charge exchange cross sections (see discussion below) and hence progress more slowly than the heavier molecular ions which do not suffer resonance charge exchange.

Figure 1 shows the drift velocities observed in the present work and Fig. 2 shows the experimentally obtained mobilities along with the expected theoretical values derived using the Langevin equation as described below. Suggested extrapolations are indicated in the figures. The log-log plots of velocity against $E/p_0$ are expected to approach a slope of one at low $E/p_0$ and $\frac{1}{2}$ at high $E/p_0$, according to an analysis by Wannier,[7] and this appears to be the case in the present work. The mobilities must be extrapolated rather far to give a zero-field reading, and the path of extrapolation is open to some question. However, zero-field mobilities with the following values and estimated uncertainties, largely arising from the extrapolation, are given in Table I.

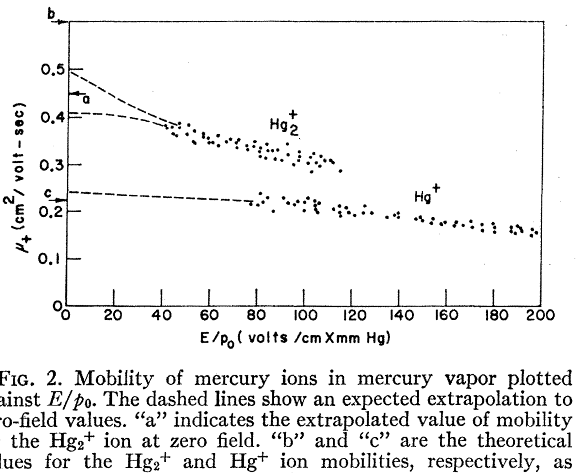

FIG. 2. Mobility of mercury ions in mercury vapor plotted against $E/p_0$. The dashed lines show an expected extrapolation to zero-field values. "a" indicates the extrapolated value of mobility for the $Hg_2^+$ ion at zero field. "b" and "c" are the theoretical values for the $Hg_2^+$ and $Hg^+$ ion mobilities, respectively, as obtained from the Langevin equation.

Insofar as the mobility itself is dependent on temperature, as opposed to any gas density effects, a temperature of the order of 500°K must be assigned to the mobility values of Table I.

### B. Secondary Electron Emission Coefficient

The Hornbeck technique used in the present experiment has the further advantage of yielding values of $\gamma_i$, the coefficient of secondary electron liberation by positive ion impact. Results show that for the molybdenum cathode, under circumstances which must be classified as "dirty," the value of $\gamma_i$ for $Hg^+$ on Mo is in the range of $5\times10^{-5}$. It has been found, however, that $\gamma_i$ can be made as large as $2\times10^{-2}$ by careful activation of the oxide-coated cathode.

## IV. COMPARISON WITH EXISTING WORK

While, as mentioned earlier, direct measurements of ionic mobilities in mercury vapor have not previously been made, there are theoretical means of predicting the mobilities as well as indirect experiments which involve mobility values. Several comparisons with the present data are described below.

### A. Studies of Afterglow Decay in Hg Discharges

Studies of the decay of afterglow in mercury discharges have led to evaluation of the diffusion coefficient for mercury ions. An early paper using this method is due to Mierdel.[8] Mierdel, however, worked in early afterglows so that he had to take into consideration elevated values of both the electron temperature and the ion temperature. He worked at pressures near 5 $\mu$ so that molecular ion formation was unlikely, when the high temperatures still prevailing and the short time intervals he used (under 100 $\mu$sec) are considered. Finally, Mierdel decided to use his findings to determine ion and electron temperatures rather than mobilities, so he was forced to insert a calculated mobility value into his equations. Without any explanation of the

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[7] G. H. Wannier, Phys. Rev. **82**, 458 (1951); **83**, 281 (1951); **87**, 795 (1952).

[8] G. Mierdel, Z. Physik **121**, 574 (1943).

TABLE I. Zero-field mobilities in mercury vapor.

| Ion | Mobility |
|---|---|
| $Hg^+$ | $0.45 \pm 0.05$ cm²/V-sec |
| $Hg_2^+$ | $0.24 \pm 0.03$ |

TABLE II. Charge transfer cross sections for $Hg^+$ in Hg vapor.

| Energy | Exptl. cross section[a] | Extrapolated Holstein theory (×2) | Cross sections linear log-log plot (×2) | Wannier and present data $Q_{\text{mob}}$ |
|---|---|---|---|---|
| 165 eV | 316 $\text{cm}^{-1}$ at 1 mm | | | |
| 75 | 351 | | | |
| 2.1[b] | | 1030 $\text{cm}^{-1}$ | 1080 | 1580 |
| 0.174[c] | | 1390 | 1460 | 1980 |

[a] See Ref. 11.

[b] $E/p_0 = 10^3$.

[c] $E/p_0 = 200$. A conversion of drift velocity to mean kinetic energy leading to the choice of the last two energies is made from Wannier's relationship $\epsilon = mv_d^2 + 3/2kT$.

value he chose other than an apology for its approximate nature, he assigned a value of 220 cm²/V-sec at 1 mm pressure, or 0.29 cm²/V-sec for the mobility constant. It may be assumed that he computed this value from the Langevin theory inserting an assumed cross section. The value must be regarded as a little high to fit with both the extrapolation of the present findings and the Langevin theory as interpreted in a later paragraph in this work. Mierdel's findings concerning temperature, using the assumed mobility, may certainly be regarded as in a reasonable range.

Dandurand and Holt[9] conducted afterglow studies in mercury discharges using spectroscopic and microwave techniques and obtained information on the method of electron removal from the discharge but simply chose Mierdel's value of the ion mobility. The present work cannot be regarded as contributing a clearcut comparison with their findings. However, in 1953, Biondi[10] made measurements on the afterglow of a mercury discharge in which helium gas was present. The helium present allowed the electrons to come to thermal equilibrium with the gas in a very short time so that microwave measurements could be made under conditions of thermal equilibrium. Assigning an equilibrium temperature of 350°K, he was able to evaluate a coefficient of diffusion for the positive ions which he published in the form $D_+ n = 1.8 \times 10^{17}$ cm²/sec (atoms/cm³). By use of the Einstein equation $\mu/D = e/kT$, a mobility may be computed from this measurement. Inserting 350°K for $T$ yields a mobility constant of 0.22 cm²/V-sec, a result accurately in agreement with the present Langevin calculation and in close agreement with our severely extrapolated experimental value.

## B. Charge Transfer Cross Sections by Direct Measurements

A completely different approach to the behavior of atomic mercury ions in mercury vapor may be made by comparison of the present data with the results on charge transfer cross sections of Palyukh and Sena.[11] While the lowest ion energy used by these writers was approximately 50 eV and the highest energy in the present work may be estimated at about 2 eV, comparisons may be made by use of Holstein's[12] theoretical work and applications of it by Sheldon.[13] Holstein has indicated that a relationship between ion kinetic energy $\epsilon$ and charge transfer cross section $Q$ for the resonant case of an ion in its parent gas should have the form

$$\epsilon = K_1 Q^{1/2} \exp(-K_2 Q^{1/2}).$$

Sheldon applied this equation using the results from Ar and Xe due to Ziegler[14] to extend the data of Kushnir *et al.*[11] in the rare gases to obtain a comparison with charge exchange data at much lower energies with very considerable success.

The mercury curve of Palyukh and Sena does not fit well with the Holstein equation. The experimental curve rises more rapidly at lower energies or less rapidly at higher energies than would be compatible with the theory. Plotting the Soviet data, even though empirical, on a log-log graph gives a better approximation to a straight line than the Holstein theory. Using the Holstein theory fitted to two experimental points, a prediction of low-energy cross sections is made in Table II. The results of the empirical extrapolation of the Soviet data as well as the present evaluations are also included in Table II; the method of reaching the present (experimental) values appears in the next paragraph.

## C. Cross-Section Calculation from Velocity Measurements

The calculation of the cross sections from drift velocity data follows a procedure due to Wannier.[7] According to this work, which has shown reasonable success as applied to the rare gases and $N_2$ and CO by Hornbeck[2] and by Varney,[3] the drift velocity $v_d$, the mean free path $\lambda$, and the ionic acceleration $a = eE/m_i$, satisfy the following relationship at high values of $E/p_0$ (above about 200):

$$v_d = 1.147 (a\lambda)^{1/2}.$$

Inserting the cross section $Q$ according to $\lambda = 1/QN$,

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[9] P. Dandurand and R. B. Holt, Phys. Rev. **82**, 868 (1951).

[10] M. Biondi, Phys. Rev. **90**, 730 (1953).

[11] B. M. Palyukh and L. A. Sena, Zh. Eksperim. i Teor. Fiz. **20**, 481 (1950). This material is reviewed and compared with newer findings by R. M. Kushnir, B. M. Palyukh, and L. A. Sena, Acad. Sci. USSR Bull. Phys. Ser. **23**, 995 (1959).

[12] T. Holstein, J. Phys. Chem. **56**, 832 (1952).

[13] J. Sheldon, Phys. Rev. Letters **8**, 64 (1962).

[14] B. Ziegler, Z. Physik **136**, 108 (1953).

TABLE III. Experimental cross sections for $Hg^+$ and $Hg_2^+$ in Hg vapor.

| Ion | $Q_{\mathrm{mob}}$ at $E/p_0=200$ cm$^2$ | cm$^{-1}$ | $Q_{\mathrm{mob}}$ at $E/p_0=1000$ cm$^2$ | cm$^{-1}$ |
|---|---|---|---|---|
| $Hg^+$ | $558\times10^{-16}$ | 1980 | $445\times10^{-16}$ | 1580 |
| $Hg_2^+$ | $137\times10^{-16}$ | 486 | $118\times10^{-16}$ | 419 (extreme extrapolation) |

where $N$ is the gas particle density, gives for $Q$

$$Q=\frac{(1.147)^2 eEkT_0}{v_d^2 m_i(p_0\times1.33\times10^3)}.$$

Absolute cgs units must be used in this equation as it stands giving $Q$ in cm$^2$. The product $QN_0$ then yields the collision probability as expressed in cm$^{-1}$ in Table II and is $3.55\times10^{16}Q$. The results expressing $Q$ in cm$^2$ and cm$^{-1}$ appear in Table III. The smaller cross sections at the higher value of $E/p_0$ more nearly satisfy Wannier's condition at high $E/p_0$.

In order to compare the directly measured charge transfer cross sections with those obtained in mobility measurements, it is necessary to note, as pointed out by Dalgarno,[15] that the cross-section value obtained from mobility measurements should be twice the value obtained from direct charge transfer.

It must be noted that Sheldon's agreements are between the extrapolated data of Kushnir *et al.* and the experimental results of Ziegler. The cross sections for charge exchange of both groups of workers are lower by factors of 2 to 2.7 than the cross sections of Varney and of Hornbeck on $Xe^+$ in Xe and $Ar^+$ in Ar, respectively, in approximate agreement with the Dalgarno observation based on Holstein's theory. The mobilities computed using the doubled cross-section values and the Langevin theory (see below) are in good agreement with the experimental measurements of mobility. It is not startling, therefore, to find the presently measured cross sections for $Hg^+$ in Hg larger, by about the same factor, than the Soviet values. Dalgarno[16] has made extensive studies of theoretical charge exchange cross sections including the case of $Hg^+$ in Hg. In Table IV a comparison of various methods is given. The present mercury cross section fits better with the Dalgarno theory than with the Palyukh and Sena extrapolated values.

### D. Theoretical Calculation of Mobility

The mobilities of $Hg^+$ and $Hg_2^+$ in Hg vapor may be computed from the Langevin theory as modernized by Hassé and Cook[17] or by a more recent calculation of Holstein,[12] limited to the resonance case. It is essential to use a collision cross section in both calculations, the cross section being essentially the hard sphere or the charge exchange value.

Polarization forces are important at lower velocities and hence the dielectric constant for mercury vapor is required in the calculation. A value for the dielectric constant derived from the atomic polarizability, in turn obtained from the Landolt-Bornstein tables[18] has been used. The computation, while intricate, is routine and is standardly shown, as for example, in Ref. 17. The results are shown in Table V. It may be noted that the Holstein calculation yields the same value of 0.22 cm$^2$/V-sec as the Langevin procedure for $Hg^+$ in Hg.

## V. DISCUSSION

The extreme degree of extrapolation of the present experimental values must be kept in mind in making comparisons. The value for $Hg^+$ seems to be slightly above the theoretical value but within the limits of expected error; that for $Hg_2^+$ is definitely and appreciably lower than the theoretical value.

It is possible that the greatest reason for the discrepancy between experimental and theoretical mobilities lies in the temperatures used experimentally. In order to reach adequate pressures to attain low values of $E/p_0$, vapor temperatures of approximately 500°K were used. The experimental values of the mobilities must be construed to be associated with the elevated temperature. The theoretical values by contrast refer to 273°K. It is emphasized that the experimental mobilities as given in Tables I and V are corrected to correspond with gas density at STP.

To the writer, it would appear that the mobility of $Hg^+$ should fall with increasing temperature and $Hg_2^+$ should rise. This conjecture is based on the mobility versus temperature studies in other gases.[4,17] Dalgarno[16] has also calculated mobilities for $Hg^+$ in Hg as a function of temperature and gives the values shown in Table VI. The values must be construed as being in good agreement with observation. Such temperature effects would

TABLE IV. Comparison of charge transfer cross sections for atomic ions in their parent gases obtained by various methods. Cross sections obtained by direct charge transfer measurements have been multiplied by a factor of 2. (See Ref. 15.) (Cross section given in units of $10^{-16}$ cm$^2$.)

| Ion | Dalgarno theory 1 eV | Dalgarno theory 10 eV | Exptl. (Hornbeck, Varney, Biondi, Kovar) (Wannier calculation) | Kushnir *et al.*; Palyukh and Sena (Sheldon extrapolation) |
|---|---|---|---|---|
| $He^+$ | 58 | 44 | 54 | |
| $Ne^+$ | 67 | 53 | 65 | |
| $Ar^+$ | 128 | 109 | 134 | 107 at 1 eV |
| $Kr^+$ | 160 | 140 | 157 | |
| $Xe^+$ | 196 | 172 | 192 | 204 at 1 eV |
| $Hg^+$ | 400 | 356 | 445 | ~327 at 1 eV |

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[15] A. Dalgarno in D. R. Bates, *Atomic and Molecular Processess* (Academic Press, Inc., New York, 1962), p. 657.

[16] A. Dalgarno, Phil. Trans. Roy. Soc. (London) **A250**, 428 (1958).

[17] See L. B. Loeb, *Fundamental Processes of Electronic Physics* (University of California Press, Berkeley, California, 1960), 2nd ed., Chap. 1.

[18] Landolt-Bornstein, *Physikalische-Chemische Tabellen* (Springer-Verlag, Berlin, 1951), Vol. I, Part 1.

augment the discrepancy between theory and experiment. It would accordingly appear from the present work that an opposite temperature effect must exist in mercury. It is interesting to note that the disagreements between theory and experiment are in opposite direction for the $Hg^+$ and $Hg_2^+$ ions. No simple systematic correction to the data can thus possibly bring both measurements into agreement with theory, an observation adding credibility to the basic validity of the experimental findings.

The primary discrepancy is, in fact, confined to the molecular ion mobility, the experimental value being significantly lower than the theoretical value. Again, this sort of disagreement has been noted in other cases, for example, $Ar_2^+$ in Ar and $He_2^+$ in He. The subject has been further confused by two different experimental values of mobility both ascribed to[19] $Ar_2^+$ and as many as three ascribed to $He_2^+$.[20–22] The experimental argument seems to have been resolved for argon in favor of the lower value for $Ar_2^+$ by McAfee[23] who identified the faster ion as $Ar^{++}$. Moreover, the results of Patterson and Beaty[20] and of Oskam *et al.*,[21] even though they differ slightly from one another, seem to strongly indicate that $He_2^+$ possesses a lower mobility rather than the higher value obtained by Biondi and Chanin.[22] A study of Dalgarno's[16] comparison of theoretical and experimental mobilities for molecular ions in atomic gases invariably gives a higher value for the theoretical result than for the experimental result, often appreciably higher. Thus, the status of the subject at this date is that the mobility of the faster ion of the present work, characterized here as $Hg_2^+$, has the additional characteristic in common with the rare-gas molecule ions of being low relative to the theoretical prediction for it.

TABLE V. Computed and experimental mobility constants in mercury.

| Ion | Experimental | Langevin theory |
|---|---|---|
| $Hg^+$ | 0.24 cm²/V-sec | 0.22 |
| $Hg_2^+$ | 0.45 | 0.60 |

TABLE VI. Temperature dependence of $Hg^+$ mobility in Hg. (Dalgarno calculation.)

| $T$ | $\mu$ |
|---|---|
| 200°K | 0.26 cm²/V-sec |
| 300°K | 0.23 |
| 400°K | 0.21 |
| 500°K | 0.19 |

Dalgarno points out that for the case of molecule ions in their parent atomic gases, at high enough temperature "$\mu$ should fall off with $T$ but the calculation is *very* sensitive to atomic parameters." If this state of affairs applies, the low experimental value for $\mu$ for $Hg_2^+$ may indeed be explained.

## ACKNOWLEDGMENT

The writer wishes to express his grateful appreciation to Professor Robert N. Varney, under whose direction the above work was carried out.

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[19] E. C. Beaty, *Proceedings of the Fifth International Conference on Ionization Phenomena in Gases, Munich, 1961* (North-Holland Publishing Company, Amsterdam, 1962).

[20] P. Patterson and E. C. Beaty, Bull. Am. Phys. Soc. **7**, 635 (1962).

[21] H. J. Oskam, V. R. Mittelstadt, J. M. Madson, R. A. Gerber, and G. F. Sauter, Bull. Am. Phys. Soc. **7**, 636 (1962).

[22] M. A. Biondi and L. M. Chanin, Phys. Rev. **108**, 1219 (1957).

[23] K. McAfee, Sixth International Conference on Ionization Phenomena in Gases, France, 1963 (unpublished).