and integrating term by term, we get

$$2B_n=\sum_{k=0}^{\infty}(2k+1)^{-1}(2k+n-1)^{-1}$$

$$+\sum_{k=0}^{\infty}(2k+1)^{-1}(2k+n+1)^{-1}-1/(n-1).$$

These sums may be expressed in terms of the logarithmic derivative of the gamma function,

$$\psi(x)=-C+\sum_{\nu=1}^{\infty}x/\nu(x+\nu),$$

and we get

$$2B_n=[1/(n-2)][\psi(n-2)-\tfrac{1}{2}\psi(n/2-1)+C/2]$$
$$+(1/n)[\psi(n)-\tfrac{1}{2}\psi(n/2)+c/2]-1/(n-1).$$

This result may be expressed as

$$B_n=\frac{n-1}{n(n-2)}\left(\tfrac{1}{2}+\tfrac{1}{4}+\cdots+\frac{1}{n-3}+\ln 2\right)-\frac{1}{2n},\quad (n\text{ odd})$$

$$=\frac{n-1}{n(n-2)}\left(1+\tfrac{1}{3}+\cdots+\frac{1}{n-3}\right)-\frac{1}{2n}.\quad (n\text{ even})$$

For $n=6$, we find $B_6=7/36$ and $J_6=7/45R_m{}^{10}$.

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Rotational Excitation and Electron Relaxation in Nitrogen*

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Using the expression given by Gerjuoy and Stein for the cross section for excitation of rotational states in N_2 by monoenergetic electrons, an exact expression for the average electron energy loss rate, $\langle dW_e/dt\rangle$, is derived in the case of a Maxwellian velocity distribution. The results are used in the interpretation of cross-modulation experiments performed at microwave frequencies in an afterglow discharge. Computed results are presented for several gas temperatures, T, in the range 300–735°K with the electron temperature, T_e, being a running variable within 250°K of the gas temperature. It is seen that $\langle dW_e/dt\rangle$ varies linearly with (T_e-T), when T_e is less than 10% in excess of T; and that the slope, proportional to the inverse electron relaxation time, τ, decreases as $T^{-1/2}$. This is also predicted by an approximate, closed form representation of $\langle dW_e/dt\rangle$, which agrees extremely well with the exact computation. The experimental data on τ, found by microwave cross-modulation techniques, agree well with theory. Using Pack and Phelps' relationship between the electron momentum transfer collision frequency ν_m, and T_e, it is found that the G factor varies at $T_e{}^{-3/2}$, with $G/G_{\text{classical}}$ ranging from 55.9 at 300°K, to 14.3 at 735°K.

INTRODUCTION

As has been suggested by Gerjuoy and Stein[1] two different approaches are feasible in order to compare the theoretically predicted cross section for rotational excitation with experimental results obtained from swarm experiments. The first approach, recently utilized by Frost and Phelps,[2] solves the Boltzmann equation with the rotational excitation terms included; and a reiteration procedure determines the collision cross sections that yield the closest fit to the presently available data on transport coefficients. In this paper, we present a second approach which is based on the cross-modulation phenomenon taking place during the afterglow of a transient, quiescent nitrogen plasma.[3] The electrons, being close to thermal equilibrium with the gas molecules, can be expected to obey a Maxwellian velocity distribution. Thus, an average value of the electron energy-loss rate can be computed and compared directly with observed data on the electron relaxation time, τ. This will also serve the purpose of determining the validity of the assumptions used for the cross-modulation experiment, namely, that the average electron energy-loss rate, $\langle dW_e/dt\rangle$, is proportional to the excess electron energy, T_e-T, T being the gas temperature.

Of particular interest, to many workers in the field of plasma diagnostics and ionospheric research, is the fractional electron excess energy loss factor, or the G factor. Apart from the cross-modulation phenomenon, which can be used as a diagnostic tool, substantial microwave heating of the electrons is often desired. In the case of the noble gases, the electron temperature for a specified field strength can be computed, since the G factor is constant (i.e., independent of the electron temperature.) In molecular gases, this is far from being the case and it is one of the purposes of the work reported here to find how the G factor varies with T_e.

* Work supported in part by the Army Missile Command and the Advanced Research Project Agency.
[1] E. Gerjuoy and S. Stein, Phys. Rev. 97, 1671 (1955).
[2] L. S. Frost and A. V. Phelps, Phys. Rev. 127, 1621 (1962).
[3] M. Mentzoni, C. Montgomery, and R. Row, Bull. Am. Phys. Soc. 7, 636 (1962).

A recent theoretical study by Dalgarno and Moffett[4] pertaining to electron cooling in the D region should be mentioned in this connection.

ELECTRON ENERGY LOSS DUE TO ROTATIONAL EXCITATION

The time rate of change of the electron energy due to rotational excitation of the diatomic nitrogen molecule is represented by[1]

$$dW_e/dt = v \sum_J N_J[\sigma_{J,J+2}(E_{J+2}-E_J) - \sigma_{J,J-2}(E_J-E_{J-2})], \quad (1)$$

where v is electron velocity, and the population of molecules in the Jth rotational state is given by[5]

$$N_J = N\frac{2B}{9kT}3(1+a)(2J+1)e^{-(B/kT)J(J+1)},$$

where N is the total molecular number density, $B(=2.49\times10^{-4}$ eV) is the rotational constant for N_2, k is Boltzmann's constant, T is gas temperature in °K, and $3(1+a)(2J+1)$ is the statistical weight with

$$a=1: J \text{ even},$$
$$=0: J \text{ odd}.$$

$\sigma_{J,J+2}$ and $\sigma_{J,J-2}$ are rotational collision cross sections for collisions of the first and second kind, respectively, given by

$$\sigma_{J,J+2} = \frac{8}{15}Q^2\pi a_0^2\left(1-\frac{B(4J+6)}{\epsilon}\right)^{1/2},$$

and

$$\sigma_{J,J-2} = \frac{8}{15}Q^2\pi a_0^2\left(1+\frac{B(4J-2)}{\epsilon}\right)^{1/2},$$

ϵ being electron energy, $Q=0.98$ is the electron quadrupole moment of the molecule in units of ea_0^2, and finally $E_J=BJ(J+1)$ is the energy of the Jth rotational state.

We want to evaluate the Maxwellian average of dW_e/dt, i.e.,

$$\left\langle\frac{dW_e}{dt}\right\rangle = \frac{1}{n}\left[\int_{v0}^{\infty}\frac{dW_{e1}}{dt}f_0dv - \int_0^{\infty}\frac{dW_{e2}}{dt}f_0dv\right], \quad (2)$$

the indices 1 and 2 represent collisions of the first and second kind, n is the electron number density, and v_0 is the lower limit of the electron velocity as determined by the cross section $\sigma_{J,J+2}$ in Eq. (1), and

$$f_0 = n(m/2\pi kT_e)^{3/2}4\pi v^2 e^{-mv^2/2kT_e}.$$

By expressing the electron velocity in terms of hyperbolic sine and cosine functions, the integrals above [see Eq. (2)] can be evaluated in closed form. The result, thus, obtained reads

$$\langle dW_e/dt\rangle = (32/\pi)^{1/2}qB^3m^{-1/2}(kT_e)(kT)^{-1}N\sum_{J=0}^{\infty}Se^{-(B/kT)J(J+1)}$$
$$\times\left[(J+2)(J+1)(2J+3)K_1\left(\frac{B}{kT_e}(2J+3)\right)e^{-(B/kT_e)(2J+3)} - J(J-1)(2J-1)K_1\left(\frac{B}{kT_e}(2J-1)\right)e^{(B/kT_e)(2J-1)}\right], \quad (3)$$

where

$$S=6: J \text{ even},$$
$$=3: J \text{ odd},$$

$q=(8/15)Q^2\pi a_0^2$, m is the electronic mass, and $K_1(z)$ is the Bessel function of the third kind.

In terms of ascending powers of z we have that[6]

$$K_1(z) = 1/z+\tfrac{1}{2}z[\ln(\tfrac{1}{2}z)+\gamma-\tfrac{1}{2}] + \tfrac{1}{16}z^3[\ln(\tfrac{1}{2}z)+\gamma-\tfrac{5}{4}], \quad \text{etc.}, \quad (4)$$

where $\gamma=0.57$ is Eulers constant. Thus, for important J levels where $z=(B/kT_e)(2J+3)\ll1$ one can use the approximation $K_1(z)=1/z$ with an error of less than 4% for $z\leqq0.4$. Furthermore, by expanding the exponentials in Eq. (3), containing J to the first power, in Maclaurin series, and converting the infinite sums to infinite integrals, one obtains

$$\langle dW_e/dt\rangle \cong 8(2/\pi)^{1/2}qBm^{-1/2}kN(kT_e)^{-1/2}(T_e-T). \quad (5)$$

Due to the smallness of the rotational quanta B, one finds an equal number of even and odd J states among the molecules above a few degrees Kelvin, a fact which is utilized in deriving Eq. (5).

Cross modulation as a way of finding the electron relaxation time is based on the relation[7,8]

$$\langle dW_e/dt\rangle + (2m/M)\nu_m\tfrac{3}{2}k(T_e-T) = G(\nu_m+\nu_{\text{rot}})\tfrac{3}{2}k(T_e-T), \quad (6)$$

where $2m/M=3.9\times10^{-5}$ is the classical value of the G factor (M is the mass of the N_2 molecule), and ν_m and ν_{rot} are the collision frequencies for momentum transfer and rotational excitation, respectively. In the electron temperature range of interest here ν_{rot}/ν_m is much smaller than unity[2] (~0.01) so that Eq. (6) can

[4] A. Dalgarno and R. J. Moffett, Planetary Space Sci. **9**, 439 (1962).
[5] G. Hertzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Inc., New York, 1950), pp. 125 and 132.
[6] G. N. Watson, *Theory of Bessel Functions* (The MacMillan Company, New York, 1948), p. 80.
[7] J. M. Anderson and L. Goldstein, Phys. Rev. **100**, 1037 (1955).
[8] V. E. Golant, Zh. Tekhn. Fiz. **30**, 1265 (1960) [translation: Soviet Phys.—Tech. Phys. **5**, 1197 (1961)].

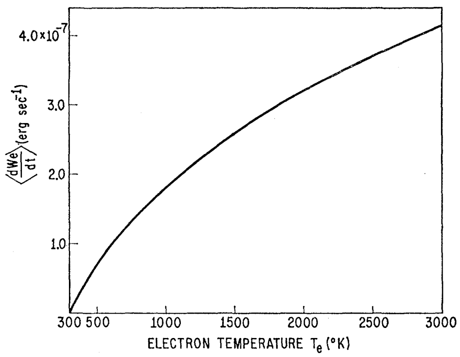

FIG. 1. Computed average electron energy-loss rate, $\langle dW_e/dt\rangle$, at a gas temperature $T=300°K$ and pressure $p=6.0$ mm Hg, vs electron temperature, T_e. The curve follows closely an approximate relation given by Eq. (5).

be written as

$$\langle dW_e/dt\rangle=(G-2m/M)\nu_m\tfrac{3}{2}k(T_e-T),\qquad(7)$$

and by combining Eqs. (5) and (7) one obtains, assuming the electrons to be Maxwellian after the application of the rf heating pulse,

$$\left(G-\frac{2m}{M}\right)\nu_m=\frac{16}{3}\left(\frac{2}{\pi}\right)^2 qBm^{-1/2}N(kT_e)^{-1/2}.\qquad(8)$$

The electron energy relaxation time, τ, following an rf heating pulse, can be found by solving an appropriate energy balance equation. The details of this computation can be found elsewhere.[7,8] It is found that $\tau\simeq(G\nu_m)^{-1}$ both for the case of $\nu_m\propto T_e^{1/2}$ and $\nu_m\propto T_e$.

The time decay of the electron energy after the removal of the dc discharge voltage pulse is of vital interest to the question of isothermal conditions. Here we can only consider the energy range below the first vibrational level (0.29 eV) where rotational excitation is the dominating electron energy loss mechanism. The very important *a priori* assumption of a linear relationship between $\langle dW_e/dt\rangle$ and (T_e-T) used for the cross modulation phenomenon has no justification in this case. However, the thermal decay for the electrons can be estimated under the assumption of the electrons obeying a Maxwellian velocity distribution, by putting Eq. (5) equal to the time derivative of the expression $\tfrac{3}{2}k(T_e-T)$. The integration of this equation yields the following expression:

$$\left(\frac{T_0}{T}\right)^{1/2}-\left(\frac{T_e}{T}\right)+\tfrac{1}{2}\ln\left[\frac{(T_0/T)^{1/2}-1}{(T_0/T)^{1/2}+1}\,\frac{(T_e/T)^{1/2}+1}{(T_e/T)^{1/2}-1}\right]=\text{const}\,\frac{Nt}{\sqrt{T}},\qquad(9)$$

where T_0 represents the initial electron temperature, which strictly speaking should not exceed 3363°K, and t is the time.

EXPERIMENTAL ARRANGEMENT AND PROCEDURE

During the present study, the plasma was contained in a quartz, cylindrical discharge tube with an inner diameter of 20 mm. The tube was about 80 cm long, and also functioned as a waveguide due to a thin layer of gold covering the outer surface. The combination discharge tube waveguide is inserted in an electron oven, so that the whole can be maintained at temperatures up to about 900°C, with no significant deterioration of the electrical properties of the waveguide, making studies at higher ambient gas temperatures possible. With regard to the electric oven, its axial heating capability was not quite uniform, and it proved to be necessary to measure the temperature (via thermocouples) both at the center and the ends of the oven, and then calculate the average.

The discharge itself was ignited on a repetitive basis by applying a dc voltage pulse, of from 1.5- to 2.5-μsec duration, between electrodes every 17 msec or so. By way of special precautions the quartz tube and electrodes were thoroughly out-gassed, initially, until residual pressure readings were 5×10^{-9} mmHg. Only ion pumps were used, and the holding pressures after overnight bake-out, prior to filling with gas to a specified pressure at all temperatures, were less than 3×10^{-8} mmHg. Commercially available flasks of Linde's spectroscopically pure nitrogen were used. Furthermore, the gas sample has to pass a liquid nitrogen cold trap before entering the discharge tube.

Details of the waveguide method of plasma diagnostics, including the cross-modulation effect, have been described elsewhere.[8] While the cw, 10-kMc/sec probing wave has to be as weak as possible so as not to disturb the plasma, the heating pulse (9.4 kMc/sec) has to be of sufficient strength to give rise to a noticeable increase in the electron temperature. The signals are operating in the quasi TE_{11} mode.[9] A narrow-band filter blocks out any direct contribution from the pulse from entering the receiver.

Additional experimental facilities include a pulse-sampling microwave radiometer,[10] added to the apparatus in the last portion of this study, permitting measurement of the electron temperature during the afterglow, and a Perkin-Elmer-112 monochromator for spectrographic studies.

RESULTS AND DISCUSSION

The results of the computation of $\langle dW_e/dt\rangle$, Eq. (3) are shown in Figs. 1 and 2. When the electron temperature T_e goes as high as 3000°K (Fig. 1) it is perhaps not justified to assume a Maxwellian distribution. However, for $T_e/T<10$ even with a Druvesteyn

[9] H. G. Unger, Bell System Tech. J. **36**, 1253 (1957).

[10] D. Formato and A. Gilardini, in *Proceedings of the Fifth International Conference on Ionization Phenomena in Gases* (North-Holland Publishing Company, Amsterdam, 1962), Vol. I, pp. 660.

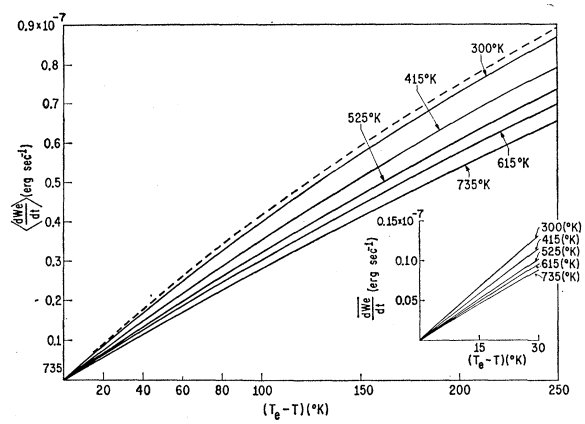

FIG. 2. Computed average electron energy loss rate, $\langle dW_e/dt\rangle$, for $p=6.0$ mmHg and various gas temperatures, T, vs excess electron temperature (T_e-T). The dashed curve represents the approximate relation given by Eq. (5) for $T=300$°K. The magnified portion of the family of curves shows how the slopes decrease with gas temperature.

distribution, the expected changes in the average will be small.[11] The actual distribution has been found to lie somewhere between the two. The computed curve in Fig. 1 follows so closely the $(T_e-T)/T_e^{1/2}$ relationship represented by Eq. (5), that if plotted, the two curves would completely overlap, except at the lowest T_e values. This indicates that collisions of the second kind, which are underestimated by the approximations made

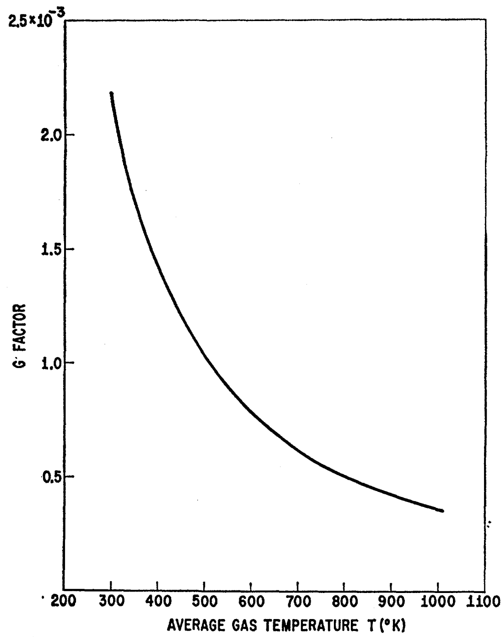

FIG. 3. The average excess fractional electron energy loss per collision, the G factor, computed from Eqs. (3), (7), and (10), vs gas temperature. The curve follows closely a $T^{-3/2}$ relationship.

[11] R. W. Crompton and D. J. Sutton, Proc. Roy. Soc. (London) **A215**, 467 (1952).

in deriving Eq. (5), are not very important, and more so the larger the ratio T_e/T. It was found, that for $T=300$°K, the contribution from the rotational states represented by $20<J\leq 40$ was less than five percent. The value $J=40$ yields a value $(B/kT_e)\times(2J+3)=0.8$ at room temperature; this value was also the basis for selecting the upper J limits for the other gas temperatures.

In Fig. 2 the electron loss rate is computed in a region of (T_e-T) pertaining directly to the diagnostic cross modulation. It is seen that $\langle dW_e/dt\rangle$ varies nearly linearly with (T_e-T) for each value of T, which is one of the basic assumptions made in writing down Eq. (6). For the ionospheric Luxembourg effect, however, the validity of this equation has been disputed.[12]

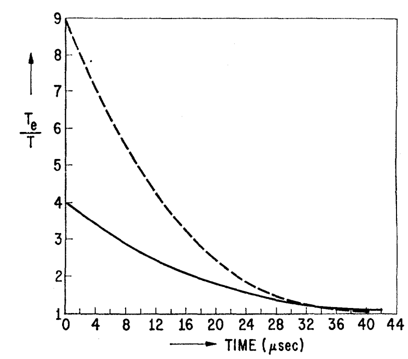

FIG. 4. Theoretical [see Eq. (9)] thermal time decay for the electrons from an initial electron temperature $T_0=3600$°K. The broken line represents $T=400$°K and $p=0.58$ mmHg; and the solid line $T=900$°K and $p=0.50$ mmHg.

As the gas temperature is increased, it is seen that the slopes of the curves in Fig. 2 decrease, and a close evaluation of them, when T_e is less than ten percent in excess of T, reveals that $G\nu_m \sim T^{-1/2}$, which from Eq. (8) indicates that $T=T_e$. Some measurements of ν_m were taken, especially at the higher gas temperatures, and these confirmed the relationship[2,13,14]

$$\nu_m = 1.3\times 10^{-7}\, N\bar{\epsilon}(\text{sec}^{-1}), \qquad (10)$$

where ϵ is the average electron energy, measured in electron volts. With this formula for ν_m, the G factor has been plotted in Fig. 3 as a function of T_e. The computed curve follows closely a $T_e^{-3/2}$ dependence and agrees also quantitatively with the approximate representation as deduced from Eqs. (8) and (10). It is noted that $G/G_{\text{classical}}$ drops from 55.9 at $T=300$°K, to 14.3 at $T=735$°K.

To illustrate how fast thermal equilibrium takes place from about vibrational threshold, due to rotational

[12] L. G. H. Huxley, Proc. Roy. Soc. (London) **A218**, 520 (1953).
[13] M. A. Biondi, in *Proceedings of the Fourth International Conference on Ionization Phenomena in Gases* (North-Holland Publishing Company, Amsterdam, 1960), Vol. I, p. 72.
[14] J. L. Pack and A. V. Phelps, Phys. Rev. **121**, 798 (1961).

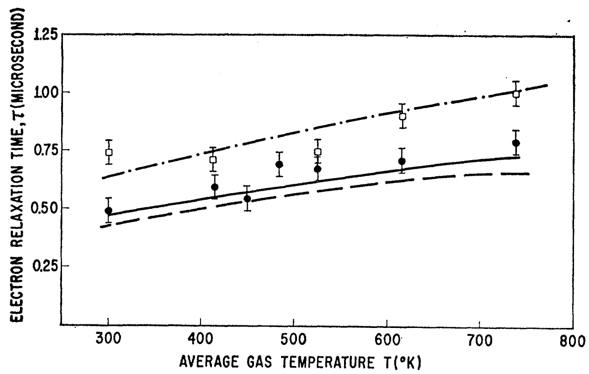

FIG. 5. Composite experimental results together with theoretically deduced curves for the electron relaxation time, τ, vs gas temperature, T. Solid dots and open squares represent experimental data taken at $p=6.0$ mmHg and $p=4.0$ mmHg, respectively. The broken and dash-dot lines are plotted from Eq. (8) for the same respective pressures; and the solid line is computed from Eqs. (3) and (7) at $p=6.0$ mmHg.

excitation only, T_e is plotted versus time in Fig. 4 according to Eq. (9) for two different gas temperatures. With our pulse-sampling microwave radiometer it was found that the total thermal decay in the electronic and vibrational energy range above 10 000°K is very fast, lasting only a few microseconds. The remaining electron temperature decay has a duration of about 20 μsec for $p=1$ mmHg and $T=300$°K, which is in reasonable agreement with theory. It should be noted that our active discharge only lasts a couple of microseconds and is driven very mildly. These are factors which may explain the discrepancy between the long-lasting, high-electron temperatures measured by Gilardini and Formato,[10] using a voltage pulse of 10 μsec, and our results.

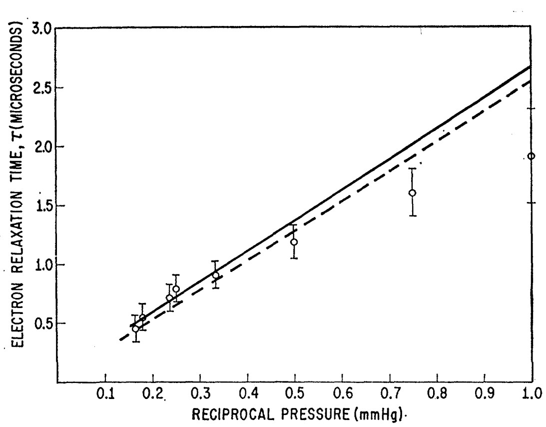

FIG. 6. Experimental results (open circles) together with curves deduced from theory for the electron relaxation time, τ, vs gas pressure, for $T=300$°K. The solid line is computed from Eqs. (3) and (7) and the broken line from Eq. (8).

The composite experimental data on the relaxation time, together with those theoretically deduced, are shown in Figs. 5 and 6. The τ values given in the figures are average values based on many interaction pulses placed at various post discharge times during the afterglow in the time interval 0.2 to about 10 msec. No systematic change of τ as a function of time is noticed; however, the depth of cross modulation increased with increasing pressure. At the lowest pressures, therefore, the necessary amplification increased the reading error considerably, as can be seen in Figs. 6 and 7. Quantitatively, it is seen that the data agree

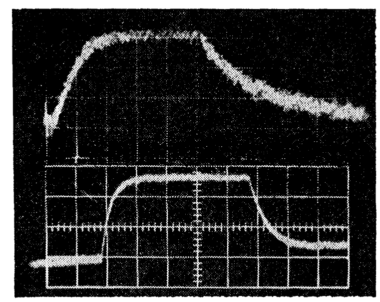

FIG. 7. Oscilloscope trace of the cross modulation for two different pressures for $T=300$°K and a post discharge time of 200 μsec, (a) $p=1.3$ mmHg, (b) $p=6.0$ mmHg.

very well with theory, in spite of the somewhat limited accuracy of the τ measurements at the lower pressures. The pressures quoted in this paper refer to 300°K.

One can, therefore, conclude that Gerjuoy and Stein's agree very well with theory, in spite of the somewhat limited accuracy of the τ measurements at the lower pressures. The pressures quoted in this paper refer to 300°K.

One can, therefore, conclude that Gerjuoy and Stein's rotational excitation theory, recently tested with regard to data on transport coefficients,[2] also agrees well with data obtained from microwave diagnostics, as shown here.

ACKNOWLEDGMENTS

The authors are grateful to Dr. C. E. Montgomery for several valuable discussions. We also want to thank J. P. Leonard for computer programming, and F. Clauson for his able assistance in carrying out the experiments.

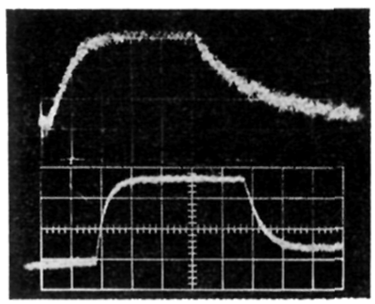

Fig. 7. Oscilloscope trace of the cross modulation for two different pressures for $T = 300°K$ and a post discharge time of 200 μsec, (a) $p = 1.3$ mmHg, (b) $p = 6.0$ mmHg.