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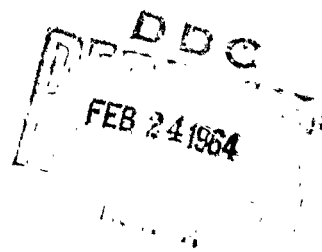
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DE-ACTIVATION OF NEON METASTABLES BY H_2

by

Thomas C. Marshall

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ABSTRACT

Measurements are reported of the total cross section for de-activation of neon $^3P_2$ and $^3P_0 (2p^5 3s)$ metastables by inelastic collisions with H_2. Measurements were made by applying the methods of resonance radiation absorption and microwave diagnostics to the afterglow plasma following a weak pulsed discharge in the mixture neon, 1mm Hg + $H_2 \approx 1\%$. The cross section for $^3P_2$ deactivation was found to increase from $0.7 \times 10^{-15} cm^2$ at 300 °K to $2.5 \times 10^{-15} cm^2$ at 650°K. The cross section for ionization of H_2 by Ne metastable $^3P_2$ collision was $0.5 \times 10^{-16} cm^2$, and was compared against similar observations for the neon-metastable + argon collision. The reaction which converts neon metastable energy into $H\alpha (6563A)$ light has been analyzed spectroscopically and forms a large fraction of the total de-activating collisions of neon metastables by H_2. These results are applied in a discussion of the effects that internal energy balance may have upon such polyatomic collisions. Observations upon DC discharge plasmas have been made and evidence collected to support and extend the above Conclusions.

TABLE OF CONTENTS

LIST OF FIGURES

I.   INTRODUCTION

In recent years the problems associated with the storage and release of energy by metastables[1], recombining atoms[2], and recombining ions[3] in active and afterglow gaseous plasmas have received increasing attention. The situation with regard to the long-lived neutral excited particles, which constitute an "impurity", is particularly challenging in plasma physics as (a) they may be present in the plasma in large concentration by virtue of their long lifetime a.id neutrality, (b) the means for detecting them is as yet semi-quantitative and awkward to apply, and (c) these particles may release their energy selectively to other constituents of the plasma in a resonance process favored by appropriate energy balance or quantum selection rules. As a practical matter, the operation of certain gaseous lasers depend on metastable-atom collisions [4,5] for a partial contribution to the population inversion of the radiating state.

We have therefore initiated a program of research directed toward understanding the production, decay, and utilization of metastable atoms during and following a gaseous discharge in neon and other noble gases. Phelps[1], in an excellent paper, has explored the processes effecting the removal of neon

metastables in a pure neon afterglow plasma of low electron density, taking into consideration electron-metastable collisions. Radiative and cumulative excitation processes effecting the production and decay of neon and helium metastables are currently under study in our laboratory. In this paper, we shall study a metastable - "impurity" collision which is especially effective in de-activating metastables of neon by one process. The hydrogen impurity was selected as it provides a physically interesting system for investigating metastable-induced molecular dissociation in a "resonance" type energy transfer reaction. Owing to the comparative simplicity of H_2, it is hoped that a theoretical investigation of particular aspects of this collision, currently in progress, will yield results of general applicability to such reactions. The issues of "energy resonance" in polyatomic collisions, viz., the concept that large inelastic type cross sections between heavy particles result when little internal energy is converted into kinetic energy, and the applicability of selection laws such as the Wigner spin conservation rule, previously found to be partly valid in atomic collisions[6], bear further consideration in slow molecular collisions. There is also the technical possibility that a gaseous discharge laser using the neon-H_2 mixture might function if the physics of metastable creation and destruction in

plasmas is better understood. Such a laser, which would operate at the Hα wavelength (6563 A), would have a unique research value.

II. PRINCIPLES OF THE Ne* - H_2 REACTION

The first group of states above the neon ground state $('S_0,$ $1s^2 2s^2 2p^6)$ belong to the configuation $2p^5 3s$, and consists of four closely spaced levels. The lowest of these, designated $Ne^*, {}^3P_2,$ lies 16.62 ev above the $'S_0$ state, and is properly metastable; its lifetime in a system of the type we shall describe is the diffustion lifetime. The level 0.052 ev above the ${}^3P_2$, the ${}^3P_1$, can radiate to the ground state by lack of pure Russell-Saunders coupling, but such radiation is self-absorbed within the plasma when the concentration of neon neutrals is $\sim 10^{17} cm^{-3}$.[1,7] The imprisonment lifetime of the ${}^3P_1 \rightarrow$ $'S_0$ radiation (743 A) has been observed by Phelps to be about 25 μsec in a long cylindrical tube of radius $\approx \frac{1}{2}$ cm at the above concentration. The ${}^3P_0$ state, .096 ev above ${}^3P_2$, is again metastable, but the $'P_1$ state, 0.23 ev above ${}^3P_2$, radiates an allowed electric dipole photon (736 A) to the $'S_0$; again this photon is radiation-trapped. The natural lifetime of the $'P_1$ state is[8] $1.2 \pm 6 \times 10^{-9} sec$, whereas Shortley[9] estimates the ${}^3P_1$ lifetime should be roughly thirteen times as great. Mixing of particles within the $2p^5 3s$ configuration can occur by

3

atomic and electronic collisions which may transfer energy ~ kT to the struck particle, or by absorption of radiation. Optical radiation, if present in high intensity, can mix the $2p^5 3s$ states by optical pumping to the ten levels of the $2p^5 3p$ configuration, followed by spontaneous emmission decays, where each excited radiating level may branch among the levels of the lower $2p^5 3s$. Our experimental work has shown that a population $\lesssim 10^{11}$ $^3P_2$ metastables per cm^3 may be obtained following an active discharge; the populations of the $^3P_1$ and $^3P_0$ states were typically $\frac{1}{5} - \frac{1}{10}$ of this, while no population could be detected in the $^1P_1$ level. In fig. 1, we show a schematic of the neon levels arranged by those of the H_2 molecule; we also give the names of the pertinant configurations in Paschen notation and their approximate energy.

The level structure of H_2 is displayed sketchily in Fig. 1 in view of the great complexity of the excited electronic terms. Although good calculation have been made for the molecular states of unexcited H_2^+ [10], the levels leading to two ground state H atoms as $r \to \infty$ [11], and those leading to $H(n=1) + H(n=2)$ [12] only experimental data[13] have been collected for the upper electronic levels. We have taken the liberty of sketching a typical binding level for the system which yields $H(n=1) + H(n=3)$ as $r \to \infty$, but have omitted the vast complexity of molecular states between that and H_2^+, which states correspond to the dissociated atoms $H + H(n \geq 4)$ as $r \to \infty$. The letter "n" refers to the principle quantum number in atomic hydrogen. The interesting feature of this system

4

is the excellent internal energy balance possible between the neon $^3P_2$ metastable and the dissociated molecule $H + H(n=3)$, which if we accepted the dissociation energy of 4.48 ev quoted by Gaydon[14], should fall only .05 ev below that energy held in the Ne* $^3P_2$.

Possible Ne* (metastable)-H_2 reactions are summarized below; we include the $^3P_{1,0}$ states because of their significant populations.

$$Ne^* + H_2 \qquad (1)$$

$$Ne + H + H(n=3) \qquad (2)$$

$$Ne^* \left\{ \begin{array}{c} ^3P_2 \\ ^3P_1 \\ ^3P_0 \end{array} \right\} + H_2 \longrightarrow \quad Ne + H + H(n=2) + 1.9\,ev \qquad (3)$$

$$Ne + H + H + 12.1\,ev \qquad (4)$$

$$Ne + H_2' \longrightarrow \left\{ \begin{array}{c} Ne + H_2 + h\nu \qquad (5) \\ Ne + H_2^+ + e^- + 1.0\,ev \qquad (6) \end{array} \right.$$

Reaction (1), elastic scattering, is very difficult to measure in our experiments because of the inelastic reactions (2)-(6), and indeed is unimportant for the loss of Ne* by diffusion as (H_2) will never exceed 2% of the neon concentration. The inelastic reactions divide into two classes, according to whether the hydrogen atoms separate or not. In reaction (3) and (4) a large amount of internal energy must be converted into kinetic energy. Emission of photons will occur as a result of reactions (2) and (3); these will by the Hα , L(yman) α and L β radiations of atomic hydrogen. With the exception of considerable Lα broadening due to the doppler effect in (3), these lines should be unperturbed by the reaction since the time for molecular dissociation ($\sim a_0/v$) is about $10^{-13}-10^{-14} sec$

whereas the time for photon emission is $\sim 10^{-7}$-10^{-9} sec in atomic hydrogen.

A physical argument,[15] commonly referenced for colliding atomic systems, suggests which of the reactions (2), (3), or (4) is most important. Suppose we regard the two systems colliding as being a classical oscillator disturbed by an impulse force $F(t)$. Only the Fourier components of $F(t)$ near the oscillator frequency ($\omega_o = \frac{E_1 - E_2}{\hbar}$) can force a disturbance. This disturbance will be large if the period of impulse, the collision time a/v, is much less than the natural period of the oscillator. Thus little excitation results unless $a/v \ll 2\pi/\omega_o$,

$$a\Delta E/hv \ll 1. \tag{7}$$

The only reaction for which even $a\Delta E/hv \sim 1$
is that of (2); the other transitions require too great a conversion of internal to kinetic energy of massive particles. Since $\Delta E \neq 0$, we expect the transition probability of (2) to increase with increasing relative velocity or gas temperature. Evidence from atom-atom collisions has been edited by Massey and Burhop[15] to establish that the increase of cross section as $\Delta E \to 0$ is appreciable and depends strongly* on the close-

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*Calculations by Stueckelberg (Helv. Phys. Acta $\underline{5}$, 370 (1932)) suggest that transfer of excitation between atomic systems is improbable for $v \sim \left(\frac{kT}{M}\right)^{1/2}$ unless $\Delta E \leq 10^{-3}$ ev.

ness of energy balance. However, the author knows of no similar evidence for polyatomic collisions.

Although we refer to (2) as a "resonance reaction", this term is customarily reserved for interactions where in addition a radiating electric dipole transition connects the excited state of each particle to the ground state. This restriction is inapplicable to our work, and thus the energy of interaction between the particles at large distance will be short range ($\sim R^{-6}$). As Bates points out,[16] this assures that the reaction will occur with a cross section which is at most gas-kinetic.

Reactions (5) and (6) are associated, as they resemble the physics of Auger transitions in atoms. In reaction (5), the H_2' de-activates by emission of one or more photons characteristic of the excited molecule. The theory of the Auger process[17] predicts that the ionization of the light molecule is $\sim 10^5$ times as probable as radiation. Thus, the lifetime for radiation being $\sim 10^{-8}$ sec, we expect a lifetime for the Auger ionization in H_2 to be $\sim 10^{-13}$ sec; hence this process is strongly competitive with (2), the favored dissociation. Reaction (6), a variation of the "Penning effect", has been observed,* but our experiments have been unable to detect any

* T.F.Moran and L.Friedman (J. Chem. Phys. $\underline{39}$ 2491 (1963))
have found that the formation of $NeH^+ + H$ is not significant.

7

molecular-hydrogen radiation from the upper electronic levels, such as the transition $4d'\Sigma_g \rightarrow 2p'\Sigma_u$ in neon-hydrogen afterglows. This is seen to be consistent with the Auger theory.

III. EXPERIMENTAL METHODS

The disposition of typical experimental apparatus is given in Fig. 2. Measurements of the total cross section for de-excitation, given by the sum over reactions (2)-(6), were made by observing the rate of decay of metastable concentration and/or $H\alpha$ light intensity following termination of a current pulse in the discharge tube. The latter was a glass tube 1 cm ID, and the current pulse required to create the plasma ranged from 10 - 50 ma for 50 - 150 μsec; the gas pressure was usually about one mm Hg. Small Tungsten wire electrodes in the tube were inert to the hydrogen fill, and the data taken on a given mixture of neon and hydrogen was the same from the first current pulse to the last. A conventional outgassed glass vacuum system where the background gas pressure was $\sim 10^{-6}$ mm Hg served for gas filling and mixing. Linde spectroscopically pure Ne, H_2, A and Matheson D_2 from a lecture bottle were used. Measurement of the minority gas concentration was made before introduction of the neon fill using an RCA 1946 thermocouple gauge that was calibrated and frequently compared against a McLeod gauge standard which, when used, was isolated from the system by cold traps. Trace impurities other than those introduced above will not influence the

8

results as the determinations did not rely in any way upon the type of heavy ion formed by the gaseous discharge.

Optical observations were made along an axial path in the afterglow about 17 cm long with a Bausch & Lomb f/5 grating spectrometer and 6217 photomultiplier detector. The low electron density in these experiments, $n_e \lesssim 3 \times 10^{10}$ electrons/cc at $t \lesssim 50$ μsec in afterglow, was responsible for the lack of electron-ion recombination light even if collected along the long optical path. Electron concentration could be measured by passing the plasma through C-band waveguide (frequency $\omega/2\pi = 4,200$ mc) and determining the microwave impedance of the system; at this frequency the plasma may be represented by a low-loss dielectric constant $\epsilon = 1 - \omega_p^2/(\omega^2 + \nu_m^2)$, where $\omega_p^2/\omega^2 = 4\pi n_e e^2/m$ and ν_m, the collision frequency for momentum transfer of electrons with neutrals, is much less than ω. These observations permitted us not only to fix the physical conditions of the afterglow to our favor, but also allowed a measure of σ_i, the cross section for ionization of H_2 by Ne* according to reaction (6). We shall discuss both optical and microwave diagnostics in detail below.

The neon oscillator strengths (f) for spectral lines terminating on the $2p^5 3s$ configuration were measured many years ago by Ladenburg,[18] who used the method of anomalous dispersion. This gave accurate relative f-numbers for the

lines; however, absolute values were obtained only after a lengthy and less rigorous argument based on gas discharge equilibria and the f-sum rule. He concluded that the oscillator strength for the $2p_q \rightarrow 1s_5$ 6402A transition was $0.5 \pm .3$. More recently,[19] further but similar experiments have shown $f = 0.26$ with 30% error, whereas W. Bennett found a lifetime for the same transition closer to Ladenburg's result. In what follows, we shall arbitrarily standardize on f=0.5 for the 6402A transition, but the choice of absolute value will seldom introduce error into our work.

The oscillator strength is related to the spontaneous emission coefficient $A_{ij} = \tau_{ij}^{-1}$ by

$$ f_{ij} \, \tau_{ij} \; = \; \frac{mc}{8\pi e^2} \; \frac{g_i}{g_j} \, \lambda_o^2 \, , \tag{8} $$

where λ_o is the wavelength of the radiation at the center of the spectral line and the subscript i pertains to the upper state. Application of the Einstein laws then shows that the integral of the frequency-dependent absorption coefficient, $k(\nu)$, of the medium is

$$ \int k(\nu) \, d\nu \; = \; \frac{\lambda_o^2}{8\pi} \, \frac{g_i}{g_j} \, \frac{N_j}{T_{ij}} \left(1 - \frac{g_j}{g_i} \, \frac{N_i}{N_j} \right) \approx \frac{\lambda_o^2}{8\pi} \, \frac{g_i}{g_j} \, \frac{N_j}{T_{ij}} \, , \tag{9} $$

the approximation applying when the density of particles in the upper state, N_i, is comparatively small. For the environmental conditions of our experiment, the neon radiation and absorption can be represented by a Doppler-broadened line

$$ k(\nu) = k_o \, exp - \{ 2(\nu - \nu_o)\sqrt{\ln 2} / \Delta\nu_o \} \equiv k_o \, exp - \Omega^2 \tag{10} $$

where $\Delta\nu_o$ is the Doppler frequency width

$$ \Delta\nu_o = \nu_o/c \, (8kT \ln 2 / M)^{1/2} \tag{11} $$

and M is the mass of the radiator. This permits a calculation for k_o:

$$k_o = \frac{2}{\Delta \nu_o} \left(\frac{\ln 2}{\pi}\right)^{1/2} \frac{\lambda_o^2}{8\pi} \frac{g_i}{g_j} \frac{N_j}{\tau_{ij}} . \tag{12}$$

We shall use a method discussed by Mitchell and Zemansky[20] for determining Nj. Low intensity spectral radiation centered at λ_o is produced by an external capillary lamp, and beamed through the medium where Nj is to be determined from the beam absorption. As the radiator and absorber are identical particles, one takes the lamp emissivity to be

$$E(\nu) = E_o \exp - (\Omega/\alpha)^2 , \tag{13}$$

where α is the ratio of the emission line width to the absorption line width. High resolution examination of the neon spectral lines emitted by a Cenco capillary lamp indeed showed the lines had a Doppler profile, but as the emitting atoms are in a plasma where fields may perturb the radiator, one cannot expect $\alpha = 1$ a priori. Measurements by Dixon and Grant[21] and Phelps[1] recommend a value of 1.5 as the most satisfactory choice; however, the nature of their data suggests that this merely tends to relieve deficiencies in the theory, particularly for large absorption, and is not necessarily indicative of the true line shape in the lamp or its subsequent absorption.

The absorption of the lamp signal in a tube of length ℓ is

$$A(\alpha, \ell) = \frac{\int_{-\infty}^{\infty} \exp - (\Omega/\alpha)^2 [1 - \exp - (k_o \ell e^{-\Omega^2})] d\Omega}{\int_{-\infty}^{\infty} \exp - (\Omega/\alpha)^2 d\Omega} , \tag{14}$$

tables of which may be found in Appendix IV of reference 20. There was little difficulty in checking our observation against these calculations; we calibrated several lines in neon ending

11

on the same state, but having different total absorption, to check consistency. Changing spectral lines is particularly useful when the absorption on a given line becomes high ($\sim$50%), as the central region of the spectral line is most sensitive to small changes in Nj and is the first region to be saturated. Graphs presented in this paper record absolute metastable concentration based upon Eq. (14) and Ladenburg's f=0.5 for the neon 6402A line. When diffusion alone controls the loss of metastables which absorb the probing radiation, the profile of metastable density should be $J_0(2.4r/R)$. However, when H_2 is introduced in quantity, the major loss mechanism is one of volume destruction, and a uniform metastable density profile must result. Since the absorption tube is long and the light beam was not collimated to a cone angle better than 2°, the experimental absorption will yield the average of metastable density across the tube diameter.

Measurements of electron density, chiefly used in the determination of σ_i, were based upon calculations of Marcuvitz[22] for a dielectric post in a waveguide. If the ratio of collision frequency to signal frequency $\nu_m/\omega \ll 1$, then

$$\left(\omega_p a\right)^2 = b^3 \omega^2 \delta /2\pi \lambda_{g_0}^2 \tag{15}$$

where a is the effective radius of the plasma tube, b is the dimension of the rectangular guide in which a TE_{01} mode propagates, λ_{g_0} is the microwave wavelength inside the waveguide, and δ is the shift in minimum of the standing waves

12

caused by introduction of the plasma. The plasma forms a
column parallel to the electric field in the guide such that
$a/b < 1/6$; the guide is shorted $\lambda_{g\circ}/4$ behind the plasma and
the position of the standing wave minimum read on a slotted line.
The ratio $2\pi\delta/\lambda_{g\circ}$ is by assumption $\ll 1$. As the afterglow
plasmas utilized here were produced by a current pulse several
electron diffusion time constants long, a fundamental electron
density diffusion mode has been established in the $J_0(2.4r/R)$
distribution at t=osec in the afterglow; this should be main-
tained as the warm electron gas cools and diffuses at low den-
sity. Thus we have calculated that the effective plasma post
is about 2/3 the plasma diameter to average the electron dis-
tribution.

This microwave technique was employed for $m\omega^2/4\pi e^2 > n_e > 10^{10} \, cm^{-3}$.
It was, however, necessary to measure electron density for $n_e < 10^{10}$
in one instance. For this, a long (55cm) quartz discharge tube
was enclosed in a X- band waveguide ($\omega/2\pi = 9400mc$) and the
electron density obtained by measuring the attenuation and
phase shift of the microwaves according to the methods of
Goldstein et al.[23] If λ_g is the microwave wavelength in the
plasma, and γ is the attenuation coefficient expressed in
nepers/m, then in MKS units the electron concentration may be
found from

$$\frac{e^2}{\epsilon_\circ m} \int n_e(r) E^2 dS \Big/ \int E^2 dS = \left(\frac{c}{\omega}\right)^2 \left[\gamma^2 + (2\pi/\lambda_{g\circ})^2 - (2\pi/\lambda_g)^2 \right], \quad (16)$$

13

where the electron distribution is to be averaged over the transverse guide dimension in the integrals involving E^2. As before, we shall quote peak (axial) values for electron concentration.

IV. FACTORS EFFECTING THE DECAY OF NEON METASTABLES

In what follows, we shall make the assumptions that the neon states $^3P_{2,1,0}$ $(2p^5 3s)$ will be converted to the $^1S_0$ state in the course of the afterglow by diffusion to the walls of the discharge tube, radiation $(^3P_1 \rightarrow {}^1S_0)$, or collision with an H_2 molecule. In view of the small radial dimension of the tube, and the low ($\sim 1 mm Hg$) gas pressure, de-activation by three body collision involving two neutrals will be neglected.[1] Metastable-metastable collisional de-activation of $^3P_2$ to the $^1S_0$ state can be ignored because of low metastable density. The thermal electron density is also low in the afterglow, but Phelps has found a large cross section($\sim 10^{-14} cm^2$) for de-activation of $^3P_0$ by $\bar{e} + Ne^*(^3P_0) \rightarrow Ne(^3P_1) + e^-$. As much more internal energy must be converted to kinetic energy to de-activate the neon to the ground state, the cross section should decrease, so we do not expect electron relaxation to be seriously competitive with diffusion loss for $n_e \lesssim 3 \times 10^{10} cm^{-3}$. However, metastable-atom and -electron collisions can readily cause an exchange of particles within the $2p^5 3s$ configuration. Thus the equations governing the concentration M,R, and S for the $^3P_{2,1,0}$ states will be coupled to each other as well as to

14

the ground state $^1S_0$ (N). The diffusion frequency, which we take to be the same for all states, is defined to be $D/\Lambda^2 \approx 3000 \ sec^{-1}$, where $D \approx 150 \ \frac{cm^2}{sec}$, obtained by Phelps' experiments.[1] We retain his notation and simplifications wherever possible, define the loss frequencies $\nu_M \equiv -\dot{M}/M$, etc, and obtain

$$\nu_M \cong D/\Lambda^2 + a\,AN(1-R/aM) + \sigma_{eM}\bar{V}(H_2) + a'A_e n_e (1-R/a'M) + b'B_e n_e (1-S/b'M) \quad (17)$$

$$\nu_R \cong \nu_{IR} + D/\Lambda^2 + AN(1- aM/R) + \sigma_{eR}\bar{V}(H_2) + e'E_e n_e (1- S/e'R) + A_e n_e(1- a'M/R) \quad (18)$$

$$\nu_S \cong D/\Lambda^2 + N(B+E) + \sigma_{eS}\bar{V}(H_2) + B_e n_e (1- b'M/S) + E_e n_e (1- e'R/S) \quad (19)$$

where ν_{IR} is the imprisoned photon decay rate from the transition $^3P_1 \to ^1S_0$ ($\sim 4\times10^4 \ sec^{-1}$), and A, B, E are the de-excitation processes for transitions $^3P_1 \to ^3P_2$, $^3P_0 \to ^3P_2$, and $^3P_0 \to ^3P_1$ either un-subscripted (for atomic collisions) or subscripted "e" (for electronic collisions). The letters a,b,e, refer to the corresponding ratios of excitation to de-excitation, and are temperature dependent: for example, at 300° K, $a = 7.1\times10^{-2}$, $b = 4.8\times10^{-3}$, $e = 5.9\times10^{-2}$. The prime on a,b,e allows for the fact that the electrons may have a warmer temperature than the atoms. The de-activation rate of metastables colliding with H_2 is $\sigma_t \bar{V} (H_2)$, where $\bar{V}$ is the average relative volocity of approach. Table I shows a typical result of adding H_2 to the gas containing neon metastables.

15

As Phelps' work has shown that the atomic mixing factors such as $AN(1- aM/R) \sim 500 sec^{-1} \ll D/\Lambda^2 \ll \sigma_e \bar{v}(H_2)$, we may neglect them in the early afterflow. Also, the decay rate in pure neon of the $^3P_0$ states is very nearly that of the more numerous $^3P_2$ states, so again we can neglect the mixing terms when at least 1/2 % H_2 is added to the neon. On the other hand, it is evident that the experimental decay time of the $^3P_1$ state greatly exceeds ν_{IR}^{-1} . We take this to be evidence of electron-induced collision mixing of $^3P_2$ states into the $^3P_1$ population since the time constant determined for electron ambipolar diffusion was also about 110 μsec. Providing we make all observations on M,R.S at early (t $\sim$ 100μsec) afterglow time, we are justified in replacing the complicated set of Eqs. (17-19) by

$$\nu_M \approx D/\Lambda^2 + \sigma_{eM} \bar{v}(H_2) \quad , \tag{20}$$

$$\nu_R \approx \nu_{IR} + \sigma_{eR} \bar{v}(H_2) + n_e A_e (1 - a'M/R) \quad , \tag{21}$$

$$\nu_S \approx D/\Lambda^2 + \sigma_{eS} \bar{v}(H_2) \quad , \tag{22}$$

where the omission of the term $a'A_e n_e (1 - R/a'M)$ from (20) follows because $M/R \gg 1$. Thus the determination of σ_e is very straightforward except in the case of Eq. (21), where there is appreciable electron interference. Taking and $M/R = 6, a' = \frac{1}{3}$ (for 1000° K electrons) with $n_{e_0} = 2 \times 10^{10} cm^{-3}$ and Phelps' value $A_e = 1.5 \times 10^{-6} cm^3/sec$, one finds a contribution of $-3 \times 10^4 \exp -t/\tau_e \; sec^{-1}$ for the third term in (21), where τ_e is the time constant of electron decay. Thus at t=0, this

16

term cancels most of μ_{IR} and yields a slope of $10^4 \, sec^{-1}$,

which is observed. We therefore report only values for σ_{tN}

and σ_{ts} . Although the former is responsible for most of

the energy transfer to H_2, σ_{ts} is also of interest since it

is farther off-resonance. The simplifications introduced above

have little to do with the accuracy of the final results,

since (20-21) are phenomenological equations.

The most interesting reaction, (2), causes the population

of the n=3 hydrogen state to change according to

$$d \, H(n=3)/dt \;=\; - \, H(n=3)/\tau_{jr} \;+\; \sigma_2 \, \bar{V} \, (H_2)(Ne^* \; ^3 P_{2,1,0}), \qquad (23)$$

where τ_{jr} is the radiative lifetime of the n=3 Bohr state,

about 10^{-8} sec,[24] and σ_2 is the partial cross section for this

process only. Since $\tau_{jr} \ll (\sigma_2 \bar{V} H_2)^{-1}$, it is apparent that

the decay of the n=3 state follows that of M. Photons are

emitted at the $L\beta$ and $H\alpha$ frequency in comparable numbers,

at a rate given by $\approx \sigma_2 \, \bar{V} \, (H_2) \, M(t)$.

V. OBSERVATIONS

Typical oscilloscope tracings are shown in Fig. 3. The

decay of the concentration of a given metastable state was ob-

tained from a partly transmitted DC light signal propagated through

the length of the afterglow column. The decay of the $H\alpha$ light

shows a corresponding slope, as will be seen quantitatively in

in Fig. 4. This lengthy decay was not detected for any other

Balmer radiation nor was it found for neon transitions (Fig. 3d)

17

which can be excited only by electronic bombardment. The rate
of fall of excitation light following the current pulse is
determined by a) direct radiative decay, b) radiative cascade
from upper levels, c) decay of very energetic electrons which
cause transitions from the ground state, and d) decay of moder-
ately energetic electrons (2 ev) which can excite radiating neon
states by cumulative excitation of the neon metastable. These
processes appear to be complete in 5 - 10 μsec, whereas the Hα
light extends ten times as long. No recombination light was
observed until the current pulse forming the afterglow was
~ 1 amp/cm^2. A theory of recombination of the ion H$^-$ by Bates
and Lewis[25] predicts selective recombination at the Hα fre-
quency; however, condensible impurities such as water vapor
were trapped out, and only these are believed to form such
negative ions in any quantity.[26] Further, if this were so, the
Hα light should fall with the time constant of the electron loss,
which was not observed.

More quantitative data are given in Fig. 4. The decay of
the $^3P_1$ states, which appears to be in good agreement with
Phelps' results, was observed with two probing radiations, the
5945 and 5882 A neon lines. The agreement of metastable con-
centration taken with the two lines is excellent. When hydrogen
is introduced, one sees that the decay rates of Hα and the
$^3P_1$ metastables match. The decay constant for M(t) was
found to be inversely proportional to the hydrogen concentration

18

when (H_2) was increased up to 2% of the neon concentration.
The temperature of the discharge tube and its surroundings
could be increased to $200^{\circ}C$ by heater tape, and an addi-
tional experiment with a hot cathode beam tube provided
experimental data at $650^{\circ}K$. The object of the beam tube
was to permit experimentation in surroundings where the
electron concentration was much lower ($n_e \sim 3 \times 10^9 \ cm^{-3}$)
and where the excited states could be produced by less potential
than in the cold-cathode discharge. The very large thermionic
cathode was responsible for the high gas temperature, but apart
from this effect the behavior of the afterglow was the same as
in the cold-cathode tube.

In table II we summarize the results for $\sigma_{\bullet M}$ and $\sigma_{\bullet S}$ for
H_2 and D_2. Deuterium was included because its electronic
structure is very similar to H_2, significant differences ap-
pearing only in the population distribution and spacing of the
rotational states. One should ovserve that 1) the cross sec-
tion increases rapidly with T, 2) the deuterium cross section
is somewhat larger than H_2, 3) the cross sections for the
$^3P_1$ and $^3P_0$ states are equal, at least within the experimental
error (about 25%). This latter fact casts some doubt on the
"resonance principle".

In view of the importance of reaction (2), we under-
took a separate but far less precise experiment to determine this
partial cross section by photon counting. The light decay of

H_λ was observed in a given volume of the afterglow with the
spectroscope (bandwidth $\sim$ 20A) and photomultiplier, both of
which had been previously calibrated against a tungsten strip-
filament lamp radiator placed in the same optical geometry.
Thus the first uncertainties lay in the calibration, where
detailed statements must be made about the emissivity of the
standard, the bandwidth of the spectroscope, and the accuracy of
the pyrometric method used to determine the standard's tempera-
ture. The second problem was to correct the measured photon
flux at the H_α wavelength for the flux lost by unobserved
ultra-violet L_β emission; to do this we made the assumptions
that a) the afterglow electrons are too cool to excite the
H_α radiation or stark-mix the fine structure of n=3, and
b) the particles placed in the n=3 state by (2) are dis-
tributed in the fine structure levels according to statistical
weights. Finally, absolute concentrations of the colliding
particles must be known. Subject to these considerable uncer-
tainties, we found the partial cross section $\sigma_2 \sim \frac{1}{3} \times 10^{-15} cm^2$,
with an estimated uncertainty of a factor of two. The value
of this observation is that now we may assert that (2) is
responsible for the lion's share of the energy transfer col-
lisions between Ne* and H_2.

Next, the fraction of σ_t which caused ionization of H_2
was investigated; reaction (6) provides a continuing source
of ionization in the afterglow which offsets partly the dif-
fusion loss, and which may be measured with microwave techniques.
Kunkel[27] has analyzed similar reactions for recombination con-

trolled afterglows. Since diffusion predominates, the loss
of electrons is given by

$$d n_e/dt = - n_e D_a/\Lambda^2 + \sigma_i \bar{v}(H_2) N_e^*(t) \tag{24}$$

where Da is the ambipolar diffusion coefficient and Ne*(t)=
$N_{mo} exp - t/T_m$ is an empiricle equation governing the rate of
decrease of metastables in the presence of H_2. This inte-
grates to

$$n_e(t) = e^{-t/T_e}\left[n_{eo} + \frac{N_{mo} \nu_i T_e T_m}{T_e - T_m}\right] - \left[\frac{N_{mo} \nu_i T_e T_m}{T_e - T_m}\right] e^{-t/T_m} , \tag{25}$$

where $T_e \equiv \Lambda^2/D_a$, $T_m^{-1} = \sigma_t \bar{v}(H_2)$, and $\nu_i = \sigma_i \bar{v}(H_2)$.

Equation (24) does not take into consideration the metastable-
metastable impact ionization, which would introduce another
term into (25) varying as $exp -2t/T_m$. Biondi's data[28] shows
this effect when $n_{eo} \sim 10^1 cm^{-3}$, whereas our data was collected
for $n_{eo} \sim 10^{10} - 10^{11} cm^{-3}$; thus we are justified in
neglecting it, and indeed it was not observed in the decay of
electron density for the pure neon afterglow (Fig. 6). Note
that T_e and T_m can be obtained from experimental data, either
from optical absorption work or the decay of electron density
given above; since $T_e > T_m$, at large time only the term
$A e^{-t/T_e}$ is significant and extrapolation to t=0 can be
used to find $\Delta n_e \equiv \frac{N_{mo} \nu_i T_e T_m}{(T_e - T_m)}$. This quantity may be used
to deduce an independent value for N_{mo} only if the ioni-
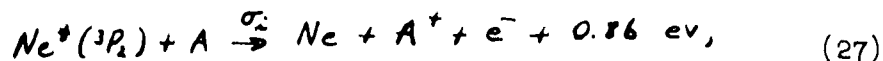zing reaction is the only way of deactivating the metastables;

21

as this was not the situation in our experiments with H_2, an independent optical absorption measurement of N_{mo} was required to find ν_i . Note Eq. (25) possesses a maximum at time

$$t' = \frac{\tau_e \tau_m}{\tau_e - \tau_m} \log \tau_e B / \tau_m A ,$$ (26)

where A pertains to the contents of the first bracket of (25) and B to the second. When $(H_2) \sim 1.5 \times 10^{14} cm^{-3}$, $\tau_m \sim 50 \mu sec$ and $\tau_e \sim 100 \mu sec$ in our equipment.

In employing Eq. (25), one tacitly assumes that the volume process of metastable-induced ionization is a perturbation upon the diffusion-controlled electron density distribution. Although the electron density is diffusion controlled at t = 0, the metastable-molecule collisions will build up the electron density profile near the walls in the early afterglow if $\Delta n_e \sim n_{eo}$. However, Δn_e is obtained operationally by extrapolation from a time $t >> \tau_m$, when the metastable ionization process has become very small. Thus Δn_e really depends on these two times only, when in each case the electron distribution is in the diffusion mode, and has been properly determined by the microwave interaction method given in Section III.

Because of the difficulty in measuring N_{mo} accurately, we decided to try the analysis first on the Penning reaction

$$Ne^{*}(^{3}P_{2}) + A \xrightarrow{\sigma_{i}} Ne + A^{+} + e^{-} + 0.86 \ ev, \tag{27}$$

where the ionization cross section can be measured in a way not depending on the absolute value of N_{mo}. In this reaction there is little doubt that the ionization cross section should dominate the de-excitation collisions because the internal energy balance for the states of argon below the ionization limit is poor, and would require a large conversion of internal energy into heavy particle kinetic energy.

From inspection of the neon metastable decay rate determined by optical absorption methods in the mixture 10 μ argon + 1 mm Hg neon, an ionization cross section of $\sigma_{i}(Ne^{*},A) = 6 \times 10^{-16} \ cm^{2}$ was determined. The effects of the ionizing source in the early afterglow were then found (Fig. 5) in this mixture as described by Eq. (25). The neon metastable decay law Ne* $= N_{mo} \, exp - t/55 \mu sec$, $N_{mo} = 2.6 \times 10^{10} \ cm^{-3}$ was obtained in the previous determination of $\sigma_{i}(Ne^{*},A)$; the absolute concentration Δn_{e} obtained from Fig. 5 then gave $\sigma_{i}(Ne^{*},A) = 8 \times 10^{-16} \ cm^{2}$, with relatively low precision $(\pm 40\%)$ because the difference $T_{e} - T_{m} \sim 15 \mu sec$ was accidentally small and depended upon the separate accuracies of the electron and metastable decay graphs. Nevertheless, the good agreement between the two methods of calculating $\sigma_{i}(Ne^{*},A)$ for this reaction provides some indirect justification for accepting the neon oscillator strength $f_{6402} = 0.5$ upon which the measurements of N_{mo} were

founded. The cross section determined by the two independent methods described lies far below that found by Kruitof and Druyvesteyn[29] (1.5×10^{-15} cm^2), above that found by Biondi[28] (2.6×10^{-16} cm^2) and Phelps and Molnar,[30] but in good agreement with the value of Schut and Smit[31] (6.7×10^{-16} cm^2).

Initial attempts to measure $\sigma_i \, (Ne^*, H_2)$ using the same apparatus met with limited success, as the ionization cross section in the neon-H$_2$ mixture was about an order of magnitude smaller than that of the neon-argon mixture. We did, however, note that the concentration of neon metastables in the after-glow was nearly independent of the current pulse when the current exceeded $\sim$ 15 ma, while the electron density increased linearly with current. Therefore, the metastable ionizing effects were made apparent by decreasing the DC pulse excitation and afterglow electron density. The post technique described in Section III was then no longer adequately sensitive, hence a new tapered discharge tube was enclosed in a 1/2 meter X-band waveguide and electron concentration measurements made according to the second technique discussed. Metastable concentration was determined prior to enclosure. In Fig. 6 it may be seen that a minimum electron concentration of 10^7 cm^{-3} could be detected, and that the ionization cross section for reaction (6), 0.5×10^{-16} cm^2 , is very much smaller than either that for Ne*-A collisions or the total deactivation cross sec-

24

tion for Ne*-H$_2$ collisions. Thus the "sensitized fluorescence" reaction (2) surely is responsible for most of σ_t , and the energy of the neon metastables is primarily transformed into light. A technical consequence of the low ionization cross section, borne out by further work reported in Section VII, is that the addition of a trace of H$_2$ to a neon discharge has little effect in increasing the electron density, unlike the Penning mixture.

VI. A MODEL OF THE Ne*-H$_2$ REACTION

The polyatomic collision Ne*-H$_2$ is very complex, and it is doubtful that even an extensive theoretical analysis of it would be conclusive. However, there are several qualitative ideas which may be applied from previous work. First, we observe that heavy particle angular momentum may be of significance in this reaction via the rotational energy term in the total Hamiltonian. Rotational barriers, occurring between the Ne* and H$_2$ particles during collision, would have a similar influence upon the reaction as those present in the formation of diatomic molecules; in a typical case, it was found that the collision diameter of the activated state of $2D = D_2$ slightly exceeds[32] that of the reaction $2H = H_2$. A "fine tuning" internal energy effect which is present in thermally activated H_2 and D_2 molecules is the somewhat different rotational level spacing and population owing to the differing

moments of inertia and nuclear spins of these electronically-
identical molecules. Thus it is not surprising to find
$\sigma_t\,(Ne^*, H_2)\,\neq\,\sigma_t\,(Ne^*, D_2)$. Long lived vibrational states[33]
of the incident H_2 or D_2 particles might also be created in-
directly by electron collision processes in the same electri-
cal discharge which generates the Ne*.

Calculations of the interaction energy between a helium
metastable (1S2S) and a helium atom $(1S^2)$,[34,35] a system having
a certain similarity to ours, have found a small energy barrier
$\sim 0.2\,eV$ which separates the free atoms from a much deeper
well. The barrier is caused by the excess valence energy at
intermediate separation, and is not from a long range resonance
interaction. The importance of a barrier, whatever the cause,
is that it permits a ready understanding of the rapid increase
of reaction probability with temperature. An activation energy
$\delta E \sim .06\,eV$, yielding a reaction rate varying as $exp\,-\delta E/kT$,
would explain the increase in σ_t reported by the experiments
at elevated gas temperature. The maximum value of σ_t for
large T would then be $\sim 5 \times 10^{-15} cm^2$. The activated molecule
$(NeH_2)^*$ may dissociate into any of the modes (1) - (6),
but the energy resonance principle could not be applied to any
channel, since $\Delta E_\alpha/h\nu > 1$. "Energy resonance" per se would
have little bearing on $\sigma_t(T)$, and the reaction cross section
$\sigma_t(T)$ for the "untuned" collisions of $Ne^*\,(^3P_\alpha) + H_2$ should

26

behave qualitatively the same as those for the better-tuned
$Ne^*(^3P_\lambda) + H_\lambda$ collisions.

The above argument casts doubt on the applicability of
the "energy resonance" principle, but it does not imply that
σ_λ must be the same as that for the other reactions (1) - (6).
Suppose we regard the Ne* - H_2 collision and reaction as being
described by the motion of a representative point on the poten-
tial energy hypersurface; the point is initially located on the
surface of Ne* + H_2, but after the collision it might be lo-
cated on that of Ne + H + H(n = 3). Since the colliding par-
ticles move with a relative speed of $\sim 2 \times 10^5 cm/sec$, if these
energy surfaces intersect or approach closely (separation <<
kT) at some point during the collision, there is a finite
probability the the sensitized fluorescence reaction will pro-
ceed. Once the representative point has been transferred to
the new surface, there is only a very small chance that it can
wander back onto the initial surface. Further, it can be
shown[36] that any two electronic terms may intersect in a
polyatomic system. An inspection of Fig. 1 suggests that
near-intersection should be the rule for practically all
electronic terms, if the particles penetrate deeply, because
of the abundance of levels in H_2 near 16 ev. But the neon
metastable, by analogy with that of helium, is certainly very
reactive, and potential energy perturbations can be expected

27

relatively far from the geometric center of the collision.
Thus inelastic reactions should occur preferentially for those
terms which intersect the initial surface a greater distance
from the force center, as these include the more frequent
grazing encounters. This argument is particularly applicable
for the terms describing $Ne^*(^3P_2) + H_2$ and $Ne + H + H(n=3)$,
which are only .05 ev apart at infinity; furthermore, repul-
sive states of $Ne + H + H(n=3)$ would probably intersect the
initial energy surface at a greater radius than the attractive
terms. Other reactions which are farther "off-resonance"
than (2) could proceed only when the colliding particles pene-
trate more deeply, and are shielded by the likelihood of a
transition (2). Thus, we can still understand how (2) could
dominate the Ne* + H$_2$ reactions, but the principles differ
from those leading to Eq. (7).

The theory of Landau and Zener[37] may be used to estimate
the velocity dependence of such non-adiabatic reactions.
Zener finds that the chance a crossing to another surface has
been made is P,

$$ P = e^{-V_0/V} , \quad V_0 \equiv 4\pi^2 \epsilon^2 / h \, |s_2 - s_1| , \qquad (28) $$

where 2ϵ is the minimum difference in separation of the two
energy hypersurfaces and $s_2 - s_1$ is the difference in slope
between the two common tangents to these surfaces. Zener has

averaged (28) over all incident velocity angles to obtain the cross section for the reaction

$$\sigma_{LZ} = \pi R_0^2 \left[e^{-v_0/v} + \frac{v_0}{v} Ei \left(-v_0/v \right) \right],$$

(29)

where R_0 is the collision radius from kinetic theory and $Ei \left(-v_0/v \right)$ is the logarithmic integral. Averaging σ_{LZ} over the Maxwellian speeds, we show in Fig. 7 a numerical plot of $\langle \sigma_{LZ} \rangle$ for what might be considered a typical choice for v_0. Recent examination of the Landau-Zener theory by Bates[38] has shown that it is much more restricted than previously believed, but that it has validity for low energy collisions.

One may summarize this discussion as follows. Although it is likely that a small Ne* - H_2 collisional barrier exists and would itself explain the temperature dependence of the total reaction, this model does not contain any obvious mechanism for favoring reaction (2), for which there is experimental evidence. However, it is very likely that a level crossing transition may occur outside the barrier owing to the very small internal energy defect in (2), and that this transition may explain the temperature dependence of σ_t through σ_2 for a select choice of level parameters.

VII. Ne* - H_2 COLLISION PROCESSES IN ACTIVE PLASMAS

Beutler and Eisenschimmel[39] observed many years ago that a small trace of H_2 in a neon discharge would yield a strong $H\alpha$

radiation. We have made observations of the Balmer light intensity, neon metastable and electronic concentrations, and the electron temperature in a conventional electrodeless discharge excited by a 40 mc rf source. The discharge tube was a long cylinder about 0.8 cm ID. Electron temperatures were determined by the method of double probes;[40] this adaptable technique is presently being refined by Aisenburg[41] and others, its fault being that it infers an electron temperature from the contribution of electrons having energies well beyond $\frac{3}{2}kT_e$. Particles in the $^3P_{2,1,0}$ states of neon were observed by monitoring the optical absorption of a variety of spectral lines terminating on these levels. Depending upon the total absorption ($\lesssim 50\%$), the probing light could be projected transverse to or along the tube axis. Since this was a cw experiment, the optical absorption sensitivity was improved by audio modulating the source lamp, and then comparing the beam transmitted through the plasma and detected with the spectroscope against the reference lamp light in a lock-in amplifier.

The theoretical and experimental ratios of absorption intensities of the $H_{\alpha,\beta,\gamma}$ radiations in an atomic hydrogen discharge are referenced by Condon and Shortley[42] as being approximately 100:20:8. To obtain the emission intensities, these values must be multiplied by the product of the pertinent level population and the cube of the decay frequency. The

relative emission intensities of the Balmer series will yield
information about a relative level population of n = 3,4,5,...
in atomic hydrogen. A photomultiplier-spectroscope was used
for these measurements, and was calibrated against a black-
body-corrected tungsten ribbon lamp to determine the absolute
detection efficiency at each of the frequencies $H_{\alpha,\beta,\gamma}$. A
mixture of $He \; 1mm + 1\%_o H_2$, for which no extraordinary He^*-H_2
dissociation and excitation is expected because of the higher
energy of the helium metastable (19.8 ev), gave an emission
ratio $H_\alpha : H_\beta : H_\gamma$ of 100:25:11. This value was obtained at low
excitation where $n_e \sim 10^{10} cm^{-3}$ and $T_e \sim 38,000 \,^{\circ}K$.

, The situation in the $Ne \; 1mm + 1\%_o H_2$ mixture was quite
different, as may be seen in Fig. 8. The emission ratio varied
from 100:6:2 at low excitation to 100:17:5 at higher power
input. The electron temperature remained relatively constant
near 32,000°K, whereas the electron density increased linearly
with discharge power over the range $5 \times 10^9 - 2 \times 10^{10} \; cm^{-3}$.
This gives conclusive evidence that the $Ne^* + H_2$ transfer
is responsible for much of the $H\alpha$ output of this discharge.
The constant $H_\beta : H_\gamma$ emission ratio is to be anticipated as
the corresponding energy levels in H_2 cannot be excited by the
Ne*. The intensity ratio $H_\alpha : H_\beta$ decreases with increasing
discharge excitation because (Fig. 9) the neon metastable
pumping rate saturates for large excitation, while the elec-

tron density and excitation increase linearly with discharge power.

Having found a region of operation where most Hα light originates by the dissociative process (2), we analyzed the spectral line for Doppler broadening. A Hilger Fabry-Perot interferometer allowed resolution of the Hα "doublet" (splitting 0.328 cm^{-1}) which is formed by the strong resolved $3^2d_{5/2} \rightarrow 2^2p_{3/2}$ and $3^2d_{3/2} \rightarrow 2^2p_{1/2}$ transitions together with weaker transitions obscured by the thermal motions of the radiating atoms. The instrument could resolve two sharp fringes produced by a visible gas laser spaced 4Gc apart. The Doppler width corresponding to H$_2$ (the system from which the excitation of Hα is derived) is about 4Gc at 300°K, while the separation of 0.328 cm^{-1} corresponds to $\Delta\nu \sim 10$ Gc. The emission from the neon-hydrogen discharge at low excitation was compared against the Hα light emitted from a hydrogen capillary tube. No difference in the line broadening or intensity was apparent, hence we conclude that an energy balance $\sim .05$ ev exothermic is certainly admissible, and that both halves of the doublet are excited equally. This amount of kinetic energy, if divided equally between the dissociating atoms, would increase the thermal Doppler broadening by $\sim 40\%$ and would be difficult to separate from the total Doppler broadening + instrumental resolution. A total linewidth of 6.5 Gc was obtained for each half of the Hα pair.

The neon metastable concentration in an electrodeless discharge in pure neon and neon 1 mm + H_2 1% is shown in Fig. 9. One should observe three facts about these results: (a) the addition of 1% H_2 reduced the population in each state by approximately the same amount; (b) the ratio M:R:S $\approx$ 4:2:1 is different from that found in the afterglow studies; (c) the concentration of neon metastables saturates at high excitation level. The result of (b) probably follows from the quantities of warm electrons found in an active plasma which may increase the population of the upper levels $^3P_{1,0}$ $(2p^5 3s)$ at the expense of the lower $^3P_2$. The saturation effect, however, bears closer examination. It can be observed with any probing neon line, and is clearly a property of the states within the discharge. We further note that it is observed in each state but that the addition of H_2 alleviates the effect. The same saturation condition occurs when the current density in a DC current discharge becomes $\gtrsim$ 50 ma/cm^2.

Three causes operate in such plasmas which may be held responsible for this effect. First, frequent electron collisions might de-excite or elevate neon metastables to other states more frequently as the electron concentration is increased. One can show that if the radiative lifetime of a typical neon upper $(2p^5 3p)$ state 2 is $\tau_{2r} \sim \frac{1}{2} \times 10^{-7}$ sec $\ll \tau_{21}$, where τ_{21} is the mean time for electron collisions which de-

excite particles to state 1, then the population ratio N_2/N_1
is

$$N_2/N_1 = \frac{g_2 \tau_{2r}}{g_1 \tau_{21}} exp - (\epsilon_2 - \epsilon_1)/kT_e .$$

(30)

Although very slow electron collisions which rearrange parti-
cles among closely separated states occur with cross section
$\sim 10^{-14} cm^2$,[1] it is very doubtful if a collision involving an
exchange of several ev would be as probable. Also, the number
of low energy ($\overline{mv^2}/2 \lesssim 0.1 ev$) electrons in a DC discharge
plasma where $T_e > 10^4 \, °K$ is less than 2% of the total. We
estimate that the electron frequency for de-excitation of the
excited atoms at concentration $n_e < 2 \times 10^{10} cm^{-3}$ could hardly
exceed $10^6 sec^{-1}$ per excited atom; thus $N_2/N_1 \sim 10^{-3}$ where
N_2 pertains to the $2p^5 3p$ and N_1 to the $2p^5 3s$ configura-
tions. Electron collisions therefore will not explain the
saturation effect either through storage of the $2p^5 3s$ parti-
cles in upper states, or by de-excitation to the $^1S_0$ ground
state of neon. The latter loss process is comparable with
diffusion loss.

A second related possibility is that Eq. (9) has been
improperly approximated for one reason or the other, and that
$g_j N_i / g_i N_j \sim 1$; this implies that the populations of the
upper levels are appreciable. However, in line with our es-

timate, both Ladenburg[18] and Pery-Thorne and Chamberlain[19] have found experimentally that this factor is $\approx 10^{-3} - 10^{-2}$ for neon discharge current below 50 ma/cm^2. Thus the ordinate of Fig. 9 represents the actual population of the states.

One common feature to the curves in Fig. 9 is that addition of H_2 to the neon, while not appreciably increasing either the charge concentration or kinetic temperature of the plasma, alleviated the saturated population effect. This again discounts the importance of electron relaxation effects. However, we have seen that the H_2 will convert the metastable energy of neon efficiently into light. For example, spectroscopic examination revealed that 1% addition of H_2 to 1 mm Hg neon effected a 50% reduction of 6402A neon radiation. From these facts we conclude that a significant fraction of the neon radiation from a hot weakly ionized plasma in the pure gas arises from cumulative excitation of the metastable "impurity" by moderately energetic electrons. This process favors the total ionization but is not useful for increasing the metastable concentration. Addition of the trace of H_2 to this plasma will remove neon metastables and favor production of higher energy electrons; these electrons will be roughly of equal effect in exciting the radiating levels of the atoms and in ionizing either Ne or H_2. On the other hand,

an over-abundance of H_2 should lower the population of electrons with energies $\gtrsim$ 16 ev, because of the lower ionization potential of H_2 and the ease of inelastic excitation of H_2 for electrons having energies > 8.8 ev.

When a steady DC current in a pure neon gaseous discharge became $\gtrsim$ 100 ma/cm^2, the population of metastables was found to be greatly reduced. When the gaseous discharge shifts into the "arc" mode of operation, it has been found that the high level of light intensity produced within the plasma may successfully store a portion of the metastable population in the upper states of neon by induced absorption and emission processes.* Electron relaxation effects also must become important when $n_e > 10^{11}\,cm^{-3}$. We therefore expect the neon metastables to play an insignificant role in controlling or sustaining an "arc" plasma.

VIII. CONCLUSIONS AND APPLICATIONS

We have seen that the addition of H_2 as an impurity to a gaseous discharge in neon will not greatly increase the level of ionization, but will effectively convert the metastable energy of the neon into the radiations cascading from the Bohr n = 3 state of atomic hydrogen. Evidence has been presented that the "sensitized fluorescent" dissociation of H_2 dominates the Ne* - H_2 deactivating collisions as might be naievely expected from the very close internal energy balance.

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* Private communication from the author's student, Mr. B. Pariser.

36

There is, however, support for the suspicion that the accuracy of the energy balance is not as critical in molecular collisions as those involving atoms only. The larger number of degrees of freedom has the effect of relaxing such selection rules as that restricting the intersection of terms in diatomic-collisions to those having different symmetry. An interpretation of the $Ne^* - H_2$ reaction has been proposed utilizing the reactivity of the metastable atom. The relevant cross sections and their temperature dependences have been measured by swarm techniques in the afterglow plasma, and indirect supporting evidence for these observations gathered from observations of hot cw weakly ionized plasmas in neon-hydrogen mixtures.

From the above investigation, we conclude that the neon-hydrogen gaseous discharge will be a reliable source of atomic hydrogen. Furthermore, inasmuch as the $Ne^* - H_2$ collision competes favorably with direct electron excitation of $H\alpha$ light even in an active descharge, this mixture deserves further consideration for an "afterglow" laser.

APPENDIX I

PROGRESS TOWARD A Ne*-H$_2$ LASER

A mixture of neutral gas and plasma will oscillate at an optical frequency[43,44] providing the gain for the desired spectral transition exceeds the losses, or equivalently

$$\alpha/\sigma_o L \quad < \quad g_1/g_2 N_2 - N_1 , \tag{31}$$

where α is the reflector system loss ($\sim 1\%$), L is the length of the optical path, N_2 and N_1 are the population densities of the upper and lower laser states, and σ_o is the peak optical cross section, obtained by solving for k_o using Eqs. (9) and (10):

$$\sigma_o = \frac{\lambda_o^3 g_2}{8\pi^{1/2} g_1 \tau_r (2kT/M)^{1/2}} . \tag{32}$$

An inspection of the matrix elements of the fine structure states comprising the n = 3 atomic hydrogen level suggests the $3^2d_{5/2}$ would be a candidate for oscillation. The $3^2d_{3/2}$ is unfortunately mixed[24] with the $3^2p_{3/2}$ owing to the small Lamb energy shift and the electric field ($\sim 2 V/cm$) which originates in the charge separation and diffusion processes inside the hot plasma. The stark mixing therefore wastes particles for both states via $L\beta$ decay. The $3^2p_{1/2}$ transition ends on the $2^2s_{1/2}$ metastable, while the oscillator strength for the $3s \rightarrow 2p$

is poor. Using data quoted in the book of Bethe and Salpeter[24], we calculate $\sigma_0 (3d_{5/2} \rightarrow 2P_{3/2}) \approx 0.3 \times 10^{-11} \, cm^2$ for deuterium. Taking the optical losses at 1%, setting $L = 10^2 \, cm$, and postulating that the $3^2 d_{5/2}$ will receive a statistical fraction (1/3) of all inelastic energy transfers with the neon metastable in reaction (2), we find the required pumping rate to this state must be supplied by $\sim 1.2 \times 10^{16}$ neon metastable deactivations $/cm^3 sec.$, if n = 2 is relatively unpopulated. Figure (9) reveals that about $2 \times 10^{15} \, cm^{-3} sec^{-1}$ is directly obtainable.

When the H_2 partial pressure is $\lesssim 10 \mu$, it is unlikely that trapping of $L\alpha$ radiation in the small diameter (1 cm) laser tube would saturate the n = 2 state. Radiation trapping of $L\alpha$ would cause the intensity of this radiation within the tube to decay with time constant[45] τ_{2r}' given by

$$\tau_{2r}'/\tau_{2r} \approx \frac{k_0 (L\alpha) R}{1.6} \sqrt{\pi \log k_0 R} \quad . \tag{33}$$

According to (33), about $3 \times 10^{13} cm^{-3}$ of atomic hydrogen may be tolerated in the tube without modifying the n = 2 lifetime. Atomic hydrogen is continuously removed at the tube walls by surface recombination. This occurs with probability[46] $\gamma_s \sim 3 \times 10^{-2}$, and the time constant for removal of H within the tube volume is accordingly

$$\left(H/\dot{H}\right)_{wl} = \left(2R/\gamma_s \overline{V}_H\right) \approx 2 \times 10^{-4} sec, \tag{34}$$

providing that the total gas pressure within the tube is sufficiently low that the atomic hydrogen is uniformly distributed. This simplification applies if the ratio of the atomic hydrogen diffusion time constant (R^2/D_H, 2.4^2) to the wall recombination constant (34) is small: $R\gamma_s \overline{V}_H/12 D_H < 1$. Thus (34) will be valid if the neon gas pressure is < 10 mm Hg. This mechanism will therefore permit the removal of atomic hydrogen at a rate of $10^{17} cm^{-3} sec^{-1}$, without interfering with the oscillation condition when τ_{2p} is used as the lifetime of the n = 2 state.

Investigation of the $H\alpha$ intensity emitted laterally from the laser tube excited by a high voltage pulse showed that the $H\alpha$ output was nearly independent of the H_2 concentration for current density $\sim 15-40$ ma/cm^2. This is the result of the constant rate of production of neon metastables in the discharge. However, as the current becomes $> 50 ma/cm^2$, the $H\alpha$ output rapidly grows as (H_2) is increased, and increases in time as well from the beginning of the excitation pulse (~ 20 μsec) to the end (~ 500 μsec). We attribute these effects to the dissociation of (H_2) in the discharge; under these conditions a sizable fraction of the $H\alpha$ intensity is caused by electronic bombardment of atomic and molecular hydrogen.

Because electron excitation is favored for levels which are radiatively connected to the ground state, it is clear that a laser action cannot occur in an environment of high energy electron ($\gtrsim 10^{11}/cc$) or hydrogen concentration. The $H\alpha/H\beta$ emission ratio of Fig. 8 suggests that at low excitation the Ne* will double the n = 3 population compared with that of n = 4 , which we assume is produced (as in n = 2) by electron bombardment only. Given the Ne* - H_2 pumping rate from Fig. 9, we deduce a total population $\sim 4 \times 10^7/cc$ for the n = 3 levels. From (30),

$$ n_3/n_2 \simeq g_3/g_2 \, \frac{\tau_{3r}}{\tau_{2r}} \, \frac{\tau_{21}}{\tau_{31}} \, e^{-(E_3 - E_2)/kT_e} ; \qquad (35) $$

the coefficient of (35) is of order unity since both $\tau_{3r, 2r}$ and $\tau_{31, 21}$ depend inversely upon the square of the matrix element connecting the n = 3 or n = 2 states with n = 1 . Thus the n = 2 population should be $\sim 2.5 \times 10^7/cc$, at least half of which, statistically, should be found in the $2\,^2P_{3/2}$ state. If the above is correct, it is clear that the population inversion between $3\,d_{5/2}$ and $2\,p_{3/2}$ is presently minute and that DC-discharge laser action is unlikely except in a tube of great length. Since the electron bombardment required to form the Ne* also creates (H), this problem cannot be sidestepped by transient DC operation. A system such as

41

the afterglow plasma, where there is no electronic excitation, appears to be the best choice.

Some semiquantitative experimental estimates of the required length of this laser were made by comparing the relative intensity of the amplified induced-emission 6328$\overset{o}{A}$ light on the axis of a 1 meter He-Ne laser just below the threshold of oscillation with the $H\alpha$-amplified light from the Ne-H$_2$ mixture. Observations were performed with the aid of interference filters and calibrated neutral-density attenuators for CW-discharge excitation consistent with the conclusions of the preceding paragraph. These recommend a tube length of at least 6 - 10 meters.

Problems of tube support, breakdown, and laboratory size indicate that a 20-foot laser tube is about the limit of useful investigation. In the next few months, a laser of these dimensions will be constructed in the Radiation Laboratories of Columbia University, where an extended optical bench of this size is available. The Ne-D$_2$ mixture in this tube will be excited by a current pulse $\sim$150 μsec duration. It can be seen that the pulse is on for a sufficient time to permit the Ne* concentration to reach equilibrium (time constant for the Ne-1 mm + D$_2$ 1% mixture $\sim$30 μsec), hence the tube will be operating under "continuous" conditions. Continuous DC current excitation must be avoided in a Ne-H$_2$ mixture because

42

of the cataphoresis effect. We expect laser action to occur, if possible, in the afterglow of the excitation pulse. Operation of the tube at elevated temperature ($\sim$500°K) will not increase the Doppler width of $H\alpha$, because of the exothermic reaction, and would require less D_2 to quench the Ne*; this would minimize high energy electron losses to H_2 by inelastic impact during the excitation pulse.

APPENDIX II

BROAD-BAND OPTICAL PUMPING OF Ne* (B. PARISER)

A preliminary experiment has shown that exposure of neon metastables, contained in an afterglow plasma, to intense broad-band light from a xenon flash tube can effect a sizable redistribution of particles in the excited levels of neon. Neon ($1S_5$) metastables were detected by monitoring the absorption of a 6402A probing beam directed down the axis of the dark afterglow plasma in neon according to the principles of Section III. At a time > 20 µs in this "afterglow," the upper excited states in neon have radiated to either the ground or metastable levels, while the electrons have become too cool for inelastic excitation. The particles in the $1S_5$ state may readily absorb radiation at the frequencies appropriate to the $1S_5 \rightarrow 2p$ transitions. As there are ten $2p$ levels, these transitions may effect an appreciable de-population of the $1S_5$ state when the stimulating radiation is intense.

A xenon flash lamp was placed parallel to the neon afterglow plasma, and the two enclosed in an optical cavity; the latter was light-tight except for small axial openings to permit the probing radiation to enter the afterglow. Owing to poor minimum resolution (~ 20 A) of the spectroscope, the flash lamp interfered with the absorption experiment; however, after the flash light had declined, one observed a persistent decrease of the $1S_5$ population. These experiments

will be repeated with a spectroscope of superior resolution ($\sim.2\overset{\text{o}}{\text{A}}$), in which much better rejection of the flash-lamp signal from the probing beam will be possible.

A mathematical model for the system was proposed; a set of 15 differential equations of the general form

$$dN_i/dt = \sum_{i \neq j} A_{ij} N_j - \sum_{i \neq j} B_{ij} U_{ij} N_i + \sum_{i \neq j} B_{ji} U_{ij} N_j$$
$$-C_i N_i \qquad (36)$$

for the 2p and 1s levels, where the A's are the spontaneous emission coefficients, the B's are the coefficients of induced absorption or emission, the U_{ij} are the energy densities obtained from the flash at the appropriate transitions, and the C_i describe the loss of the $1S$ metastable particles by diffusion. Transitions from the $^1S_0$ to the $3S$ levels were neglected as no ultraviolet was passed by the glass discharge tube. Initially the ground state was assumed to have about $10^{16} cm^{-3}$ population and the $1S$ to have $10^{11} cm^{-3}$. The population of the $1S$ was normalized to unity at $t = 0$. The set of Eqs. (36) was solved on an IBM 7090 computer using the method of Laplace transforms, after a radiation density equivalent to a black body at $5700^{\circ}K$ in the spectral range $5000 - 7000\overset{\text{o}}{\text{A}}$ was assumed. This figure was arrived at by spectroscopic comparison of the flash intensity with a blackbody standard. The oscillator strengths measured by Ladenburg were used for this calculation.

Typical results are shown in Fig. 10, where the
particles have been exposed, at t = 0, to a flash suddenly
rising to the above intensity. It is seen that the ratio of
$2p_1/1s_5$ remains constant from 10^{-7} to 10^{-4} sec at a value of
2.7%. Thus a significant quenching of the $1s_5$ population may
result during the flash; afterwards, branching decays from
the 2p levels to the $1s_4$ and $1s_2$ levels will cause the net
decrease of $1s_5$ owing to de-activation of the $1s_4$ and $1s_2$
by more rapid radiative decay. Further experimental and
theoretical work is in progress.

APPENDIX III

INITIATION OF A THEORETICAL STUDY APPROPRIATE

TO A Ne*-H$_2$ COLLISION (L. SIEGEL)

A quantitative description of a Ne*-H$_2$ collision in-
volves two distinct problems. First, a reasonable model for
the Ne*-H$_2$ interaction must be assumed and the interaction
potential derived. We are convinced that this problem is
soluble by the methods of molecular quantum mechanics, but
that the solution could be very tedious and have limited
application. The second problem involves the scattering of
the particles in this derived potential. A review of the
classic work of Mott and Massey, Wu, and Bates has shown
that little quantitative work has been done in the area of
slow atomic collisions. The general solution leads to a set
of coupled differential equations, which is ordinarily approx-
imated by neglecting all interactions except that between the
initial and final states. The validity of this two-state
approximation has been challenged by Bates; however, the
available information is so sketchy that it is frequently
difficult to estimate the error introduced by neglect of
coupling terms.

One solution of the two-state approximation leading to
a closed-form result is that of Landau-Zener. A preliminary
review of this theory has shown that it may be applicable to

slow "resonant" collisions of the Ne^*-H_2 or He^*-Ne type. A
quantitative study of the accuracy of the Landau-Zener approx-
imation for collisions of this type is in order and the feasi-
bility of such an investigation is under consideration.

TABLE I

TIME-VARYING BEHAVIOR OF THE Ne* $2p^5 3s$ IN THE AFTERGLOW

State	1.2 mm Pure Ne			1.2 mm Ne+1.2×10^{14}cm^{-3}H$_2$		
	M	R	S	M	R	S
Rel. Pop. at 50 µsec in Afterglow	1	1/6	1/6	1	1/6	1/10
Exp. Decay Const. at 50 µsec in Afterglow (µsec)	340	115	280	65	55	60

TABLE II

SUMMARY OF EXPERIMENTAL RESULTS, TOTAL CROSS SECTION
FOR DE-ACTIVATION OF Ne* BY COLLISIONS WITH H$_2$

Reaction	T°K	Cross Section σ_t, in 10^{-15} cm^2
Ne^{3}P$_2$ + H$_2$	300	0.7
Ne^{3}P$_2$ + H$_2$	500	1.5
Ne^{3}P$_2$ + H$_2$	650	2.5
Ne^{3}P$_2$ + D$_2$	300	1.1
Ne^{3}P$_2$ + D$_2$	500	1.7
Ne^{3}P$_0$ + H$_2$	300	0.7
Ne^{3}P$_0$ + H$_2$	500	1.6

Fig. 1

50

Fig. 2

51

H_α LIGHT DECAY

DECAY OF DISCHARGE
NEON 6599Å LIGHT

PULSE

↕20μs
PULSE

TRANSMISSION

PULSE

D.C. NEON
LIGHT

H_β LIGHT DECAY

↕20μs
PULSE

Fig. 3

52

Fig. 4

ELECTRON DENSITY DECAY
NEON 1.0 mm + ARGON 10μ

$$n_e(t) = e^{-t/\tau_e}\left[n_{eo} + \frac{N_{mo}\nu_i\tau_e\tau_m}{\tau_e-\tau_m}\right] - \frac{N_{mo}\nu_i\tau_e\tau_i}{\tau_e-\tau_m}\ e^{-t/\tau_m}$$

$Ne^* + A \rightarrow A^+ + Ne + e^-$

$\sigma_i \approx 0.8 \times 10^{-15}\ cm^2$

n_{eo}

ELECTRON CONCENTRATION/cc

10^{11}
10^{10}

t (μsec)

0   50   100   150   200   250   300

Fig. 5

54

$$\sigma_i (Ne^*, H_2) = 0.5 \times 10^{-16}\ cm^2$$

$$N_m(t) = 6.7 \times 10^{10}/cc\ e^{-t/50\mu s}$$

PURE NEON DECAY
1 mm
(PULSE i = 40 ma)

1 mm NEON +
1.5 x 10^{14}/cc H_2
(PULSE i = 10 ma)

Δn_e

ELECTRON DENSITY, cc^{-1}

t (μ sec)

Fig. 6

$$\langle\sigma_{LZ}\rangle_v = \langle\pi R_0^2 \{ e^{-v_0/v} + \frac{v_0}{v} Ei(\frac{-v_0}{v}) \}\rangle_v$$

$v_0 = 1.5 \times 10^5 \text{cm/sec}$

Fig. 7

56

INTENSITY RATIOS : I_α / I_β ———⊙———
I_β / I_γ ----□----

RF DISCHARGE IN 1MM NEON + 10μH$_2$

RELATIVE POWER INPUT
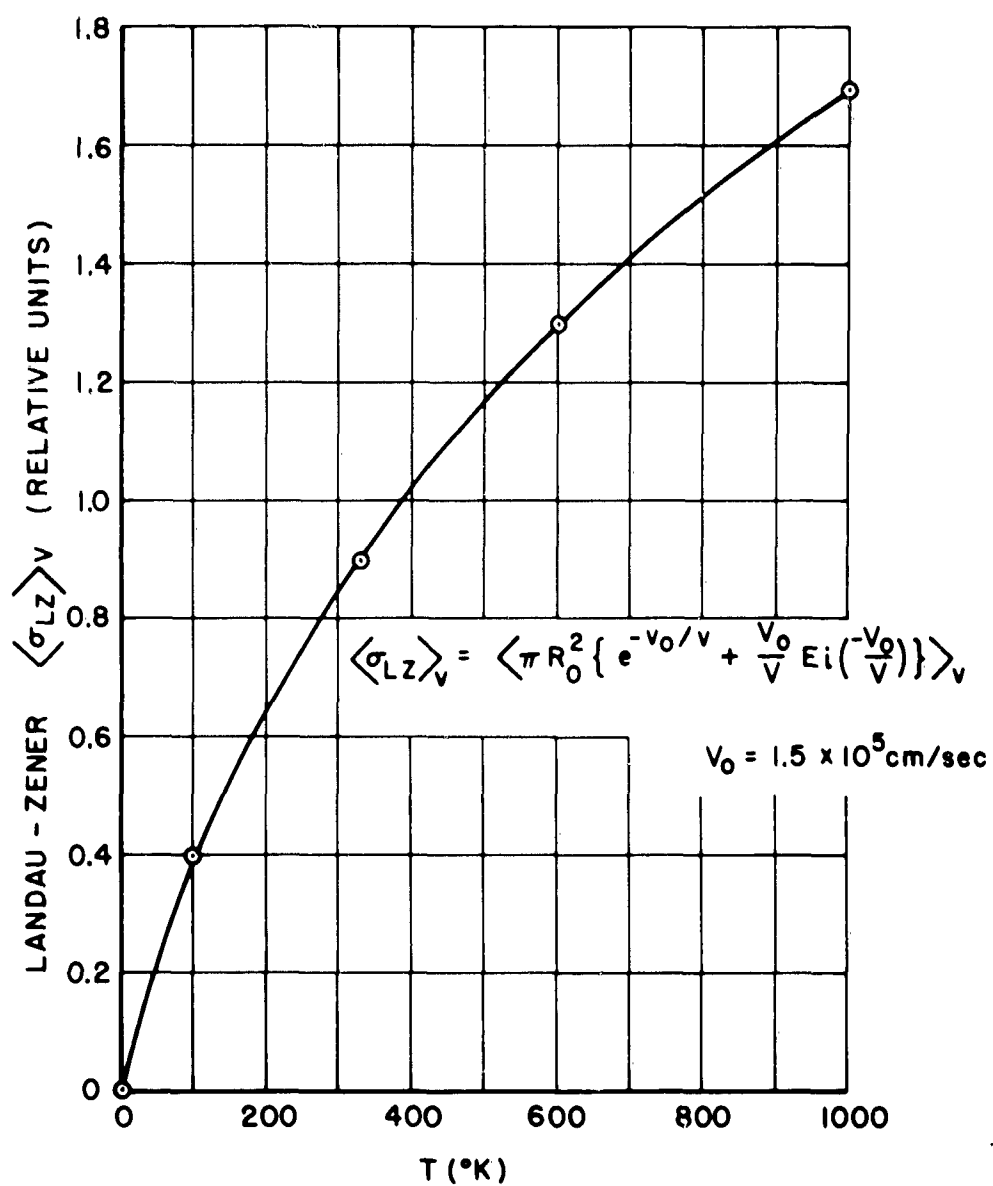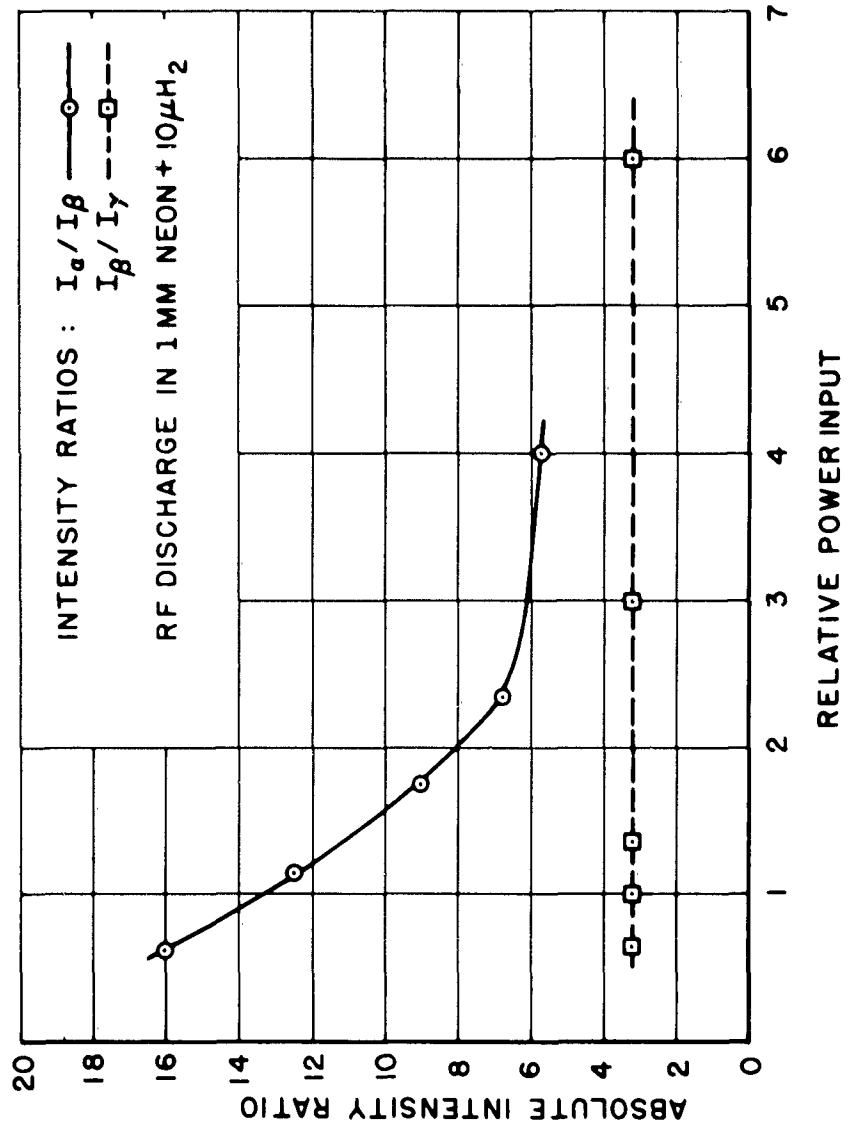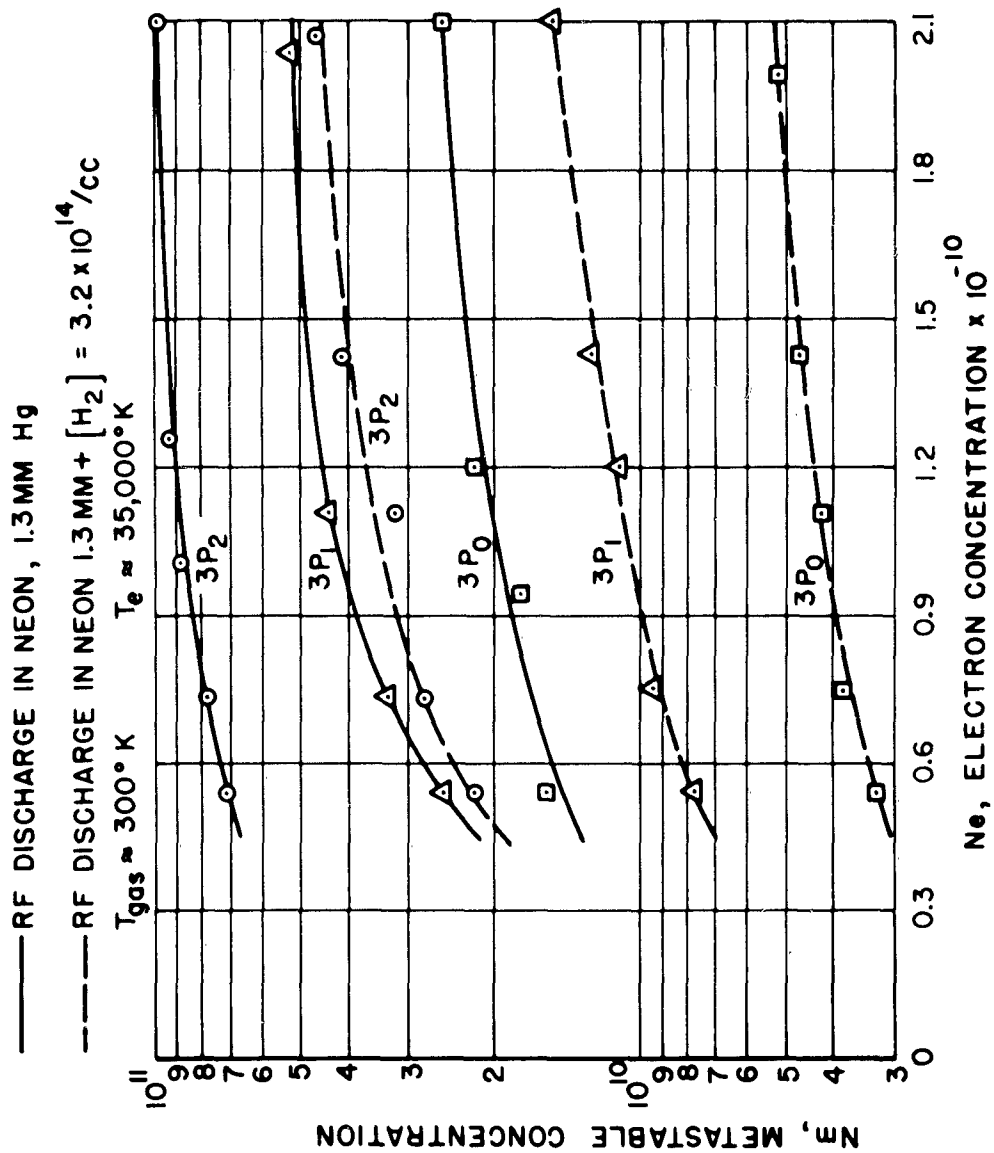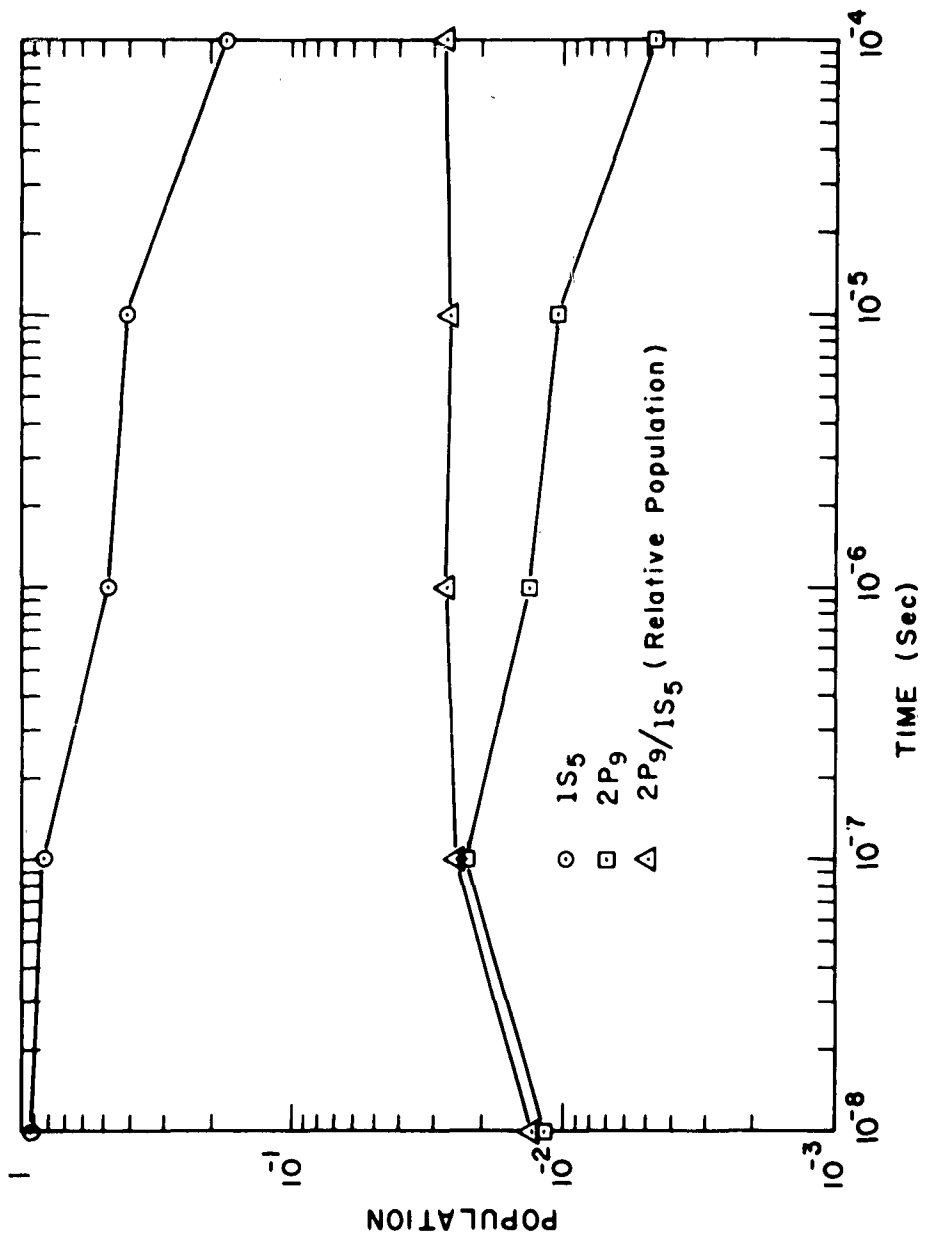
ABSOLUTE INTENSITY RATIO

Fig. 8

Fig. 9

Fig. 10

PREDICTED POPULATIONS OF EXCITED LEVELS IN NEON DURING XENON FLASH, TEMP 5700°K

REFERENCES

1. A. V. Phelps, Phys. Rev. 114 1011 (1959).
2. T. Marshall, IEEE Trans. Nuclear Sci. NS-10, 124 (1963.
3. J. M. Anderson, GE report No. 61-RL-2817G, Sept. 1961. (review article).
4. A. Javan, W.R. Bennett, Jr., and D. R. Herriott, Phys. Rev. Letters 6 106 (1961).
5. W. R. Bennett, Jr., W. L. Faust, R. A. McFarlane, and C. K. N. Patel, Phys. Rev. Letters 8 470 (1962).
6. H. S. W. Massey and E. H. S. Burhop, "Electronic and Ionic Impact Phenomena, p. 427 et. reg., Oxford (1952).
7. T. H. Holstein, Phys. Rev. 72 1212 (1947).
8. W. Schütz Ann Physik 18 705 (1933) and H. Schillbach Ann Physik 18 721 (1933).
9. G. H. Shortley, Phys Rev. 47 295 (1935).
10. E. A. Hylleraas, Z physik 71 739 (1931).
11. H. M. James and A. S. Coolidge, J. Chem. Phys. 1, 825 (1933).
12. A. S. Coolidge and H. M. James, J. Chem. Phys. 6, 730 (1938).
13. O. W. Richardson, "Molecular Hydrogen and its Spectrum," Oxford (1934) and H. Beutler, A. Deubner, H. O. Junger, Z.f Physik 98, 181 (1935).
14. A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules, London, Chapman and Hall (1953) p. 225.
15. Massey and Burhop, op. Cit., p. 441.
16. D. R. Bates, "Atomic and Molecular Processes," Academic Press (1962) p. 615.
17. E. H. S. Burhop, "The Auger Effect," Cambridge 1952, p.48.
18. R. Ladenburg, Revs. Modern Phys. 5 243 (1933).

19. A. Pery-Thorne and J. E. Chamberlain, Proc. Phys. Soc. (London) 82, 133, (1963); also, W. R. Bennett, Jr., Appl. Optics Suppl., (Jan. 1962) p. 41.

20. A. C. G. Mitchell and M. W. Zemansky, "Resonance Radiation and Excited Atoms," Cambridge (1961), p. 121 et. seq.

21. J. R. Dixon and F. A. Grant, Phys. Rev. 107 118 (1957).

22. N. Marcuvitz, "Waveguide Handbook" v. 10 McGraw-Hill (1951) p. 266.

23. L. Goldstein, M. A. Lampert, R. H. Geiger, Elect. Commun. Sept. 1952, p. 243.

24. H. A. Bethe and E. E. Salpeter, "Quantum Mechanics of One- and Two - Electron Atoms," Academic (1957), p. 266 and 290.

25. D. R. Bates and J. T. Lewis, Proc. Phys. Soc. A68 173 (1955)

26. H. S. W. Massey, "Negative Ions," Cambridge (1950)p. 81.

27. W. B. Kunkel, Phys. Rev. 84 218 (1951).

28. M. A. Biondi, Phys. Rev. 88, 660 (1952)

29. A. A. Kruithof and M. J. Druyvesteyn, Physica 4, 450 (1937).

30. A. V. Phelps and J. P. Molnar, Phys. Rev. 89 1202 (1953).

31. G. Schut and J. A. Smit, Physica 10, 440 (1943).

32. S. Glasstone, K. J. Laidler, H. Eyring, "The Theory of Rate Processes," McGraw-Hill, p. 127 (1941).

33. J. D. Lambert, "Relaxation in Gases," in D. R. Bates, "Atomic and Molecular Processes," Academic Press, p. 783 (1962).

34. R. Buckingham and A. Dalgarno, Proc. Roy. Soc. (London) A213 327 (1952).

35. G. H. Bridgman, S. J. Brient, and F. H. Matsen, J. Chem. Phys., 34 958 (1961).

36. L. D. Landau and E. M. Lifshitz, "Quantum Mechanics," Addison-Wesley (1958), p. 265.

37. C. Zener, Proc. Roy. Soc. (London) A137, 696 (1932).

38. D. R. Bates, Proc. Roy. Soc. A257, 22 (1960).

39. H. Beutler and W. Eisenschimmel Z. Physik Chem. B10, 89,(1930).

40. E. O. Johnson and L. Malter, Phys. Rev. 80 , 58,(1950).

41. S. Aisenberg, Appl. Phys. Letters 2, 187, (1963

42. E. U. Condon and G. H. Shortley, "The Theory of Atomic Spectra," Cambridge (1959), p. 139.

43. B. A. Lengyel, "Lasers," Wiley (1962).

44. A. L. Schawlow and C. H. Townes, Phys. Rev. 112, 1940 (1958).

45. T. H. Holstein, Phys. Rev. 83, 1159 (1951).

46. K. E. Shuler and K. J. Laidler, J. Chem. Phys. 17, 1212 (1949).