# Neon Transition Probabilities*

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Relative transition probabilities for 12 visible neon lines originating on the $3s_2$ and $3s_3$ (Paschen notation) levels of neon have been measured. The experimental technique utilizes the interaction between the output of a helium–neon laser oscillating at 3.39 $\mu$ ($3s_2$–$3p_4$) and the excited atoms in a neon discharge. Changes of intensity of spontaneous emission from the $3s_2$ and $3s_3$ levels result from this interaction. By analyzing these intensity changes as a function of pressure, we have determined the ratio of the transition probabilities for the $3s_2$–$3p_4$ and the $3s_2$–$2p_5$ transitions. This ratio is 7.10±0.57. The measurements also yield the product of the radiative lifetime of the $3s_3$ level and the effective cross section for transfer of excitation between the $3s_2$ and $3s_3$ levels. This product is $\tau_3\sigma_{23}=(9.93\pm0.80)\times10^{-23}$ sec-cm². The transition probabilities are placed on an absolute scale by use of a recently reported absolute value for the $3s_2$–$2p_4$ transition. The experimental values are compared with the theoretically calculated transition probabilities for which a *j-l* coupling model was used. This comparison points out the rather large departure of these levels from *j-l* coupling.

INDEX HEADINGS: Atomic spectra; Neon; Laser.

THE development of the laser has presented spectroscopists with a powerful tool with which specific atomic and molecular energy levels can be selectively probed. In particular, it is often difficult to find conventional sources of sufficient intensity to excite higher-lying levels, particularly those levels not optically connected to the ground state. For those levels between which laser action can take place, laser excitation of these levels should prove fruitful for the study of such parameters as lifetimes and transition probabilities.

Using a method developed by Parks and Javan,[1] we have measured relative transition probabilities for 12 visible transitions originating from the $3s_2$ and $3s_3$ (Paschen notation) levels of neon. The same measurements which yield the ratio of the transition probabilities also yield the product of the radiative lifetime of the $3s_3$ level and the effective collision cross section for excitation transfer between the $3s_2$ and $3s_3$ levels.

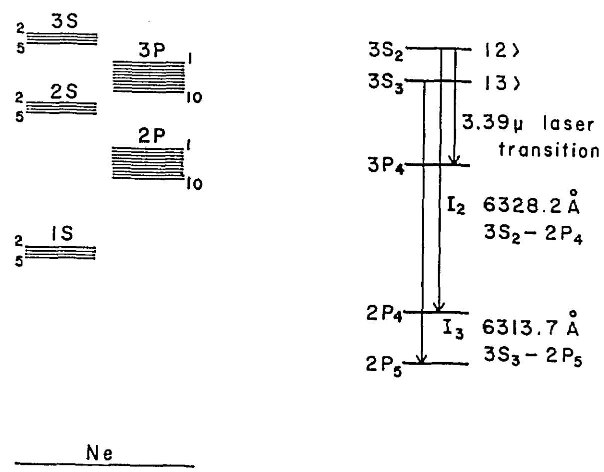


FIG. 1. Simplified neon energy-level diagram.

## THEORY

We present here a brief review of the theory developed in Ref. 1. When the output of a helium–neon laser oscillating on the 3.39-$\mu$ $3s_2$–$3p_4$ transition (see Fig. 1) passes through a neon discharge, the population of the $3s_2$ level is increased by the partial absorption of the radiation. Since the $3s_3$ level lies only 50 cm⁻¹ below the $3s_2$ level, the population density of atoms in the $3s_3$ level also increases because of collision excitation transfer. The collisions responsible for the excitation transfer are

$$\mathrm{Ne}_a(3s_2)+\mathrm{Ne}_b(0)\rightleftarrows\mathrm{Ne}_b(3s_3)+\mathrm{Ne}_a(0)+\mathrm{K.E.}$$
$$\mathrm{Ne}_a(3s_2)+\mathrm{Ne}_b(0)\rightleftarrows\mathrm{Ne}_a(3s_3)+\mathrm{Ne}_a(0)+\mathrm{K.E.}$$

In the following discussion, the $3s_2$ and $3s_3$ levels are denoted by $|2\rangle$ and $|3\rangle$, respectively. Consider the rate equation for the steady-state population of the $3s_3$ level,

$$\frac{dn_3}{dt}=-\frac{n_3}{\tau_3}+\frac{n_2}{\theta_{23}}-\frac{n_3}{\theta_{32}}+R_3=0. \tag{1}$$

Here $n_3$ is the population density of level $|3\rangle$, $n_2$ is the population density of level $|2\rangle$ which is the upper laser level, $\tau_3$ is the radiative lifetime of level $|3\rangle$, $1/\theta_{23}$ is the collision rate for a process involving a nonradiative transition from $|2\rangle$ to $|3\rangle$, $1/\theta_{32}$ is the collision rate for the inverse process, and $R_3$ is the net rate of population change of level $|3\rangle$ by all remaining processes. Assuming that the net rate $R_3$ is not affected by the presence of the laser radiation, we obtain the difference between Eq. (1) and the steady-state rate equation for the

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[1] J. H. Parks and A. Javan, Phys. Rev. 139, A1352 (1965).

$3s_3$ level in the presence of laser radiation,

$$-\frac{\Delta n_3}{\tau_3}+\frac{\Delta n_2}{\theta_{23}}-\frac{\Delta n_3}{\theta_{32}}=0, \quad (2)$$

where $\Delta n_3$ and $\Delta n_2$ are the changes induced in the population of the $3s_2$ and $3s_3$ levels as the laser is switched on and off. The collision rate $1/\theta_{32}$ can be related to an effective cross section as follows

$$1/\theta_{32}=n_0 v_r \sigma_{32}.$$

Here $n_0$ is the density of the ground-state atoms, $v_r$ is the relative thermal speed between colliding atoms, and $\sigma_{32}$ is the effective cross section. The crucial point in the theory of Ref. 1 is that the ratio $\theta_{32}/\theta_{23}$ is given by

$$\theta_{32}/\theta_{23}=(g_3/g_2)\exp[(E_2-E_3)/kT] \quad (4)$$

if the velocity distribution of the ground-state atoms and the excited atoms in levels $|2\rangle$ and $|3\rangle$ is maxwellian at some temperature $T$. Thus at pressures high enough that $\theta_{32}\ll\tau_3$, we obtain from Eq. (2)

$$\Delta n_3/\Delta n_2=(g_3/g_2)\exp[(E_2-E_3)/kT]. \quad (5)$$

Experimentally, we observe changes of intensity of the spontaneous emission from levels $|2\rangle$ and $|3\rangle$ as the laser is switched on and off. The ratio of the changes of intensity, $\Delta I_3/\Delta I_2$, is given by

$$\Delta I_3/\Delta I_2=(A_3\nu_3/A_2\nu_2)(\Delta n_3/\Delta n_2), \quad (6)$$

where $A_3$ and $A_2$ are transition probabilities for transitions from $|3\rangle$ and $|2\rangle$ at frequencies $\nu_3$ and $\nu_2$. Thus by measuring $\Delta I_2/\Delta I_3$ in the region of pressure where Eq. (5) is applicable, we obtain the ratio $A_2/A_3$. For purposes of analysis, we rewrite Eq. (2) in the form

$$\begin{aligned}\Delta n_2/\Delta n_3&=\theta_{23}/\tau_3+\theta_{23}/\theta_{32}\\&=(1/n_0 v_r \sigma_{23}\tau_3)+(g_2/g_3)\exp[(E_3-E_2)/kT]. \quad (7)\end{aligned}$$

Using Eq. (6) and substituting $p=n_0kT$ in Eq. (7), we obtain

$$\frac{\Delta I_2}{\Delta I_3}=\left[\frac{A_2\nu_2kT}{A_3\nu_3v_r\sigma_{23}\tau_3}\right]\frac{1}{p}+\left[\frac{A_2\nu_2g_2}{A_3\nu_3g_3}\right]\exp\left[\frac{E_3-E_2}{kT}\right]. \quad (8)$$

Thus, if we know the temperature, we can find the ratio $A_2/A_3$ and the product $\sigma_{23}\tau_3$ by plotting the measured ratios $\Delta I_2/\Delta I_3$ against the reciprocal of the pressure and fitting the points with a straight line. The intercept of this line yields the ratio $A_2/A_3$ and from the slope we can find the product $\sigma_{23}\tau_3$. Within the limits of experimental error we can take the temperature to be 400 K.

## EXPERIMENTAL DETAILS

The experimental arrangement is shown in Fig. 2 and is basically the same as that in Ref. 1. This arrangement allows a direct determination of $\Delta I_3$ and $\Delta I_2$.

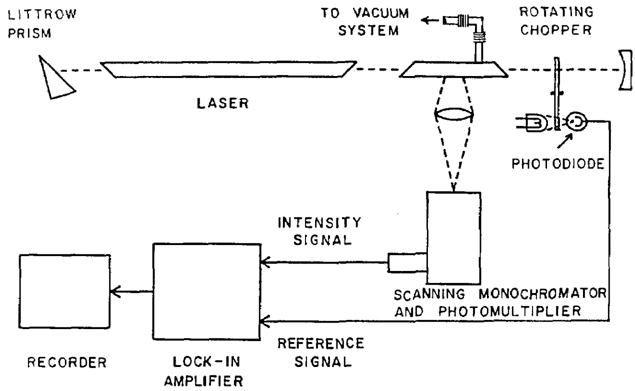


FIG. 2. Experimental arrangement.

This is accomplished by switching the laser beam on and off by use of a rotating chopper within the cavity while the spontaneous emission is monitored from the side of the small discharge tube. In order to obtain the greatest possible signal-to-noise ratio, the small discharge tube is placed within the laser cavity, where the laser radiation field is about two orders of magnitude greater than that obtainable outside the cavity. To minimize loss, the small discharge tube is built with quartz Brewster-angle windows. In order to vary the pressure, the small discharge cell is connected to a high-vacuum system and a pure-gas-handling system.

The side light from the small discharge cell was focused on the entrance slit of a half-meter grating spectrometer and detected with a photomultiplier. The detected signal is then sent to a lock-in amplifier. The output of the lock-in amplifier is directly proportional to the change of the detected signal as the laser is switched on and off.

It is necessary to eliminate any oscillation which might begin or end in level $|3\rangle$ or produce radiative cascade into level $|3\rangle$. To do this, we have taken advantage of the extremely high gain of the $3s_2$–$3p_4$ transition. As one of the reflectors, we have used a Littrow prism, which limits oscillation to a narrow wavelength region about 3.39 $\mu$. At the other end of the cavity, at a distance of 2 m from the prism reflector, is a spherical gold mirror whose radius of curvature is 1 m. This combination of mirror–radii and separation results in a high-loss cavity.[2] However, because of the large gain at 3.39 $\mu$, oscillation still takes place, with essentially no loss of signal. Other laser transitions in the neighborhood of 3.39 $\mu$ (which have much lower gain) are suppressed, however, because of the large cavity loss. The detection system was calibrated by use of an EOA quartz iodine standard lamp.

## RESULTS AND DISCUSSION

Figure 3 is a plot of the experimentally measured ratio $\Delta I_2/\Delta I_3$ vs the reciprocal of the pressure. The

[2] G. D. Boyd and H. Kogelnik, Bell System Tech. J. 41, 1364 (1962).

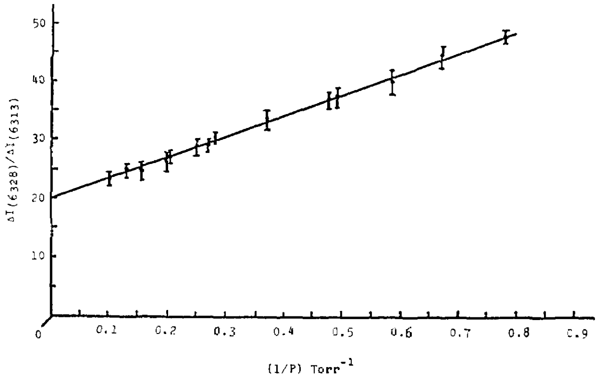


FIG. 3. Intensity-change ratio $\Delta I_2/\Delta I_3$ is plotted against the reciprocal of the neon pressure. The line is the least-squares fit to the data, a=20.31, b=35.85.

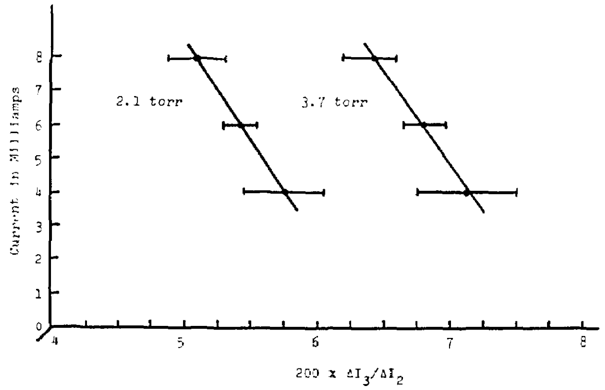


FIG. 5. Intensity-change ratio $\Delta I_3/\Delta I_2$ as a function of current.

solid line is the least-squares fit to the data. Figure 4 is a plot of the same data, in which however, the ratio $\Delta I_3/\Delta I_2$ is plotted directly against the pressure. From Fig. 4 we note that the ratio $\Delta n_3/\Delta n_2$ is essentially thermalized above 10 torr.

The simple form of Eq. (2) results from two assumptions. The first assumption is that in the rate equation for the $3s_3$ level, we have ignored the contribution of excitation from the $3s_4$ and $3s_5$ levels as well as the $4d$ levels of neon. Neglect of these terms is not strictly justified. We have detected collision transfer from the $3s_2$ level to $3s_4$, $3s_5$, and $4d$ levels. However, an analysis of a rate equation similar to Eq. (1) but including the contribution of transfer from these nearby levels yields only second-order correction terms proportional to the cross section squared and therefore negligible in the low-pressure region. The correction to the high-pressure region is also within experimental error.

The second simplifying assumption is taking the rate $R_3$ to be unchanged in the presence of the radiation field. Suppose $R_3$ contains a term describing excitation of the $3s_3$ level owing to electron collisions with atoms in an excited state. Suppose further that the population of this excited state depends on the population of either the upper or lower laser level or both. Then the rate $R_3$ will not have the same value in the presence of laser radiation as it did in the absence of the radiation. Including such a term in $R_3$ and assuming the electron density to be proportional to the current and proceeding in the same manner used to derive Eq. (2), we obtain

$$\frac{\Delta n_3}{\Delta n_2}=\left[\frac{1}{\tau_3}+\frac{1}{\theta_{32}}\right]^{-1}\left\{\frac{1}{\theta_{23}}+\frac{\Delta n_4}{\Delta n_2}ki\right\}.$$

Here $\Delta n_4$ represents the change in population of some excited level whose total population depends on the population of either the upper and/or lower laser level. $K$ is a proportionality constant and $i$ is the current in the discharge tube.

Thus the ratio $\Delta I_3/\Delta I_2$ should be proportional to the current at any particular pressure. We have observed such an effect. Figure 5 is a plot of $\Delta I_3/\Delta I_2$ vs the current for two different pressures. From the slope of the curve in Fig. 5, we can deduce that the population of the effective level decreases as the laser is switched on. In order to account for this current-dependent term in $R_3$, we have determined the constants of the straight-line fit to Eq. (8) for a number of different currents and have extrapolated their values

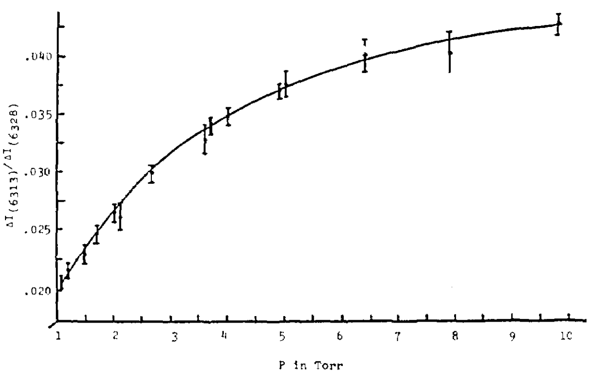


FIG. 4. Intensity-change ratio $\Delta I_3/\Delta I_2$ plotted against the neon pressure.

TABLE I. Relative transition probabilities measured in this experiment compared with theoretically calculated transition probabilities from $L$–$S$ coupling and $j$–$l$ coupling models. Relative probabilities normalized on the $3s_2$–$2p_5$ transition.

| | | Relative transition probabilities | | |
|---|---|---|---|---|
| Transition | λ | $L$–$S$ | $j$–$l$ | Experimental |
| $3s_2$–$2p_1$ | 7304.8 | 2.13 | 6.40 | 4.35 |
| $3s_3$–$2p_2$ | 6421.7 | 0 | 9.41 | 4.82 |
| $3s_2$–$2p_3$ | 6351.9 | 0 | 0 | 5.38 |
| $3s_2$–$2p_4$ | 6328.2 | 0 | 49.19 | 54.35 |
| $3s_3$–$2p_5$ | 6313.7 | 0 | 59.43 | 7.65 |
| $3s_2$–$2p_5$ | 6293.8 | 10.00 | 10.00 | 10.00 |
| $3s_2$–$2p_6$ | 6118.0 | 18.15 | 0 | 9.51 |
| $3s_3$–$2p_7$ | 6064.6 | 18.63 | 0 | 3.74 |
| $3s_2$–$2p_7$ | 6046.2 | 0 | 0 | 3.53 |
| $3s_2$–$2p_8$ | 5939.3 | 0 | 0 | 3.04 |
| $3s_3$–$2p_{10}$ | 5448.5 | 2.05 | 0 | 1.06 |
| $3s_2$–$2p_{10}$ | 5433.7 | 0 | 0 | 4.13 |

to zero current. After extrapolation to zero current, the results are

$$A_{(3s_2-2p_4)}/A_{(3s_3-2p_5)}=7.10\pm0.057$$
$$\tau_3\sigma_{23}=(9.93\pm0.80)\times10^{-23}\ \text{sec}-\text{cm}^2.$$

Table I presents relative transition probabilities for other visible transitions originating on the $3s_2$ and $3s_3$ levels. Included in this table is a comparison of the relative transition probabilities predicted by both $L$–$S$ coupling and $j$–$l$ coupling models. It is clear that $j$–$l$ coupling is a closer description of the actual coupling scheme in neon than is $L$–$S$ coupling. It is also clear, however, that $j$–$l$ coupling is not an adequate model for calculating transition probabilities for these levels. These transitions may be placed on an absolute scale using a recently measured value for the $3s_2$–$2p_4$ transition.[3] The absolute value, however, depends on the value of the transition probability for the $2p_4$–$1s_4$ transition which was measured by Ladenburg. The uncertainty of the absolute value of this transition probability is on the order of 20% to 30%. Thus the uncertainty of the measured absolute value of the $3s_2$–$2p_4$ transition probability is of at least this value.

Table II lists the absolute transition probabilities for the transitions considered in this experiment based on the value given for the $3s_2$–$2p_4$ transition in Ref. 4. The probable errors indicated in Table II do not include the error of the absolute value of the $3s_2$–$2p_4$ transition probability.

[3] Th. Hansch and P. Toschek, Phys. Letters **20**, 273 (1966).

TABLE II. Absolute transition probabilities for visible neon transitions originating on the $3s_2$ and $3s_3$ levels.

| Transition | λ | $A\times10^{-6}$ sec. |
|---|---|---|
| $3s_2$–$2p_1$ | 7304.8 | 0.41±0.06 |
| $3s_3$–$2p_2$ | 6421.7 | 0.45±0.07 |
| $3s_2$–$2p_3$ | 6351.7 | 0.50±0.07 |
| $3s_2$–$2p_4$ | 6328.2 | 5.1 ±0.7 |
| $3s_3$–$2p_5$ | 6313.7 | 0.72±0.11 |
| $3s_2$–$2p_5$ | 6293.8 | 0.94±0.13 |
| $3s_2$–$2p_6$ | 6118.0 | 0.89±0.13 |
| $3s_3$–$2p_7$ | 6064.6 | 0.35±0.06 |
| $3s_2$–$2p_7$ | 6046.2 | 0.33±0.05 |
| $3s_2$–$2p_8$ | 5739.3 | 0.29±0.04 |
| $3s_3$–$2p_{10}$ | 5448.5 | 0.10±0.02 |
| $3s_2$–$2p_{10}$ | 5433.7 | 0.39±0.06 |

In conclusion, we point out that finding two levels conveniently spaced such as the $3s_2$ and $3s_3$ levels of neon is not an unusual occurrence in noble gases (with the exception of helium). This is the result of the $j$–$l$ coupling tendency of the neon configuration and the configurations of the heavier noble gases. We also note that this experimental technique could be used for the study of electron–atom collisions such as are described by Eq. (9).

G. J. Chamberlin (Tintometer Ltd., England) and E. Ganz (Ciba A. G., Switzerland) at meeting of Experts on Colorimetry of International Commission on Illumination, Washington, D. C., 15 June 1967.

W. Schultze (BASF A. G., Ludwigshafen, Germany) and A. Brockes (Bayer A. G., Bayer-Leverkusen, Germany) at meeting of Experts on Colorimetry of International Commission on Illumination, Washington, D. C., 15 June 1967.