Energy-transfer processes in decaying neon-copper gaseous plasmas

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Light-absorption and -emission spectroscopy were used in the studies of the time dependencies of the Cu II spectral emission, Ne I spectral emission, and $Ne^m(^3P_2)$ and $Cu(4s\ ^2S_{1/2})$ densities in the stationary afterglow of a sputtered Ne-Cu hollow cathode discharge. Transitions from 16 Cu II energy levels were monitored in the afterglow. The three Cu II levels between 21.16 and 21.41 eV are produced, either directly or by cascading, by charge exchange between Ne^+ and Cu. The one Cu II level at 19.58 eV is predominantly produced by charge exchange between Ne_2^+ and Cu. The remaining Cu II levels are produced by both reactions. No evidence was found for the production of Cu II excited states by the Penning ionization of Cu by $Ne^m(^3P_2)$. A value of $220\pm8\ cm^2\ sec^{-1}$ Torr was measured for the diffusion coefficient of $Cu(4s\ ^2S_{1/2})$ in neon.

I. INTRODUCTION

Recently many studies[1–4] have been done involving rare-gas–metal-vapor laser action. These studies have indicated that the upper laser levels, which are the excited states of the singly ionized metal ion, are populated via two excitation processes. These are the thermal-energy charge-transfer reaction

$$R^+ + M \rightarrow R + (M^+)^* + \Delta E \quad (1)$$

and the Penning-ionization reaction

$$R^m + M \rightarrow R + (M^+)^* + e + \Delta E\ , \quad (2)$$

where R, R^+, and R^m denote, respectively, the ground-state atom, ground-state ion, and the rare-gas atom in a metastable state. M and $(M^+)^*$ denote, respectively, the ground-state metal atom and excited metal ion, and ΔE is the energy defect. Investigations of reaction (1) have shown that the reaction rate is largest for $0<\Delta E<0.6$ eV.[5–7] For reaction (2) there are indications that Penning ionization cross sections increase with increasing energy defect.[7]

Reactions (1) and (2) have been studied extensively for systems involving various combinations of rare gases and higher-vapor-pressure metals. However, few studies have been done on energy-transfer reactions between rare gases and lower-vapor-pressure metals. One such study was recently performed in our laboratories on the He-Cu system.[8] While this study confirmed the importance of reaction (1), no evidence was found for the production of excited ion states by the Penning reaction (2) for this system. The experimental work reported here was undertaken in an effort to further explore this discrepancy with previous results. The Ne-Cu system was chosen for the present investigation for two reasons. First, the sputtering rate of Cu by a rare gas is the largest for any metal.[9] Therefore, based on our previous studies and since the sputtering rate of Cu by neon ions is larger than by helium ions, a sufficient metal-vapor density can be achieved in the discharge region solely by sputtering at the cathode. Second, as can be seen in Fig. 1, there is a good energy coincidence between the active neon species and various Cu II levels. This energy coincidence can result in energy-transfer processes involving the thermal-energy charge-transfer reactions

$$Ne^+ + Cu \rightarrow Ne + (Cu^+)^* \quad (3)$$

and

$$Ne_2^+ + Cu \rightarrow 2Ne + (Cu^+)^*\ , \quad (4)$$

and the Penning-ionization reaction

$$Ne^m + Cu \rightarrow Ne + (Cu^+)^* + e\ , \quad (5)$$

where Cu is the ground-state copper atom $Cu(4s\ ^2S_{1/2})$.

This paper presents measurements relating to processes (3)–(5) in the stationary afterglow of the Ne-Cu hollow cathode discharge. These measurements were performed using light-emission and -absorption spectroscopy. In order to determine which reaction is responsible for the production of a specific excited state of the singly ionized copper atom, careful stationary afterglow studies were done on the time-dependent densities of the ground-state

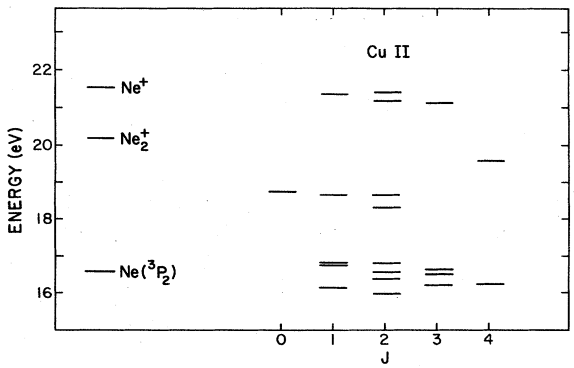

FIG. 1. Energy-level diagram for Ne^+, Ne_2^+, $Ne^m(^3P_2)$, and monitored Cu II energy states. Only the lowest vibrational level ($v=0$) is included for Ne_2^+.

copper atoms and various active neon species and on the time dependencies of the emission intensities from various Cu II energy levels. The results of these studies indicated which specific energy-transfer processes were responsible for the production of the Cu II energy levels. In addition, from these data, the diffusion coefficient of $Cu(4s\ ^2S_{1/2})$ in neon was also obtained.

II. EXPERIMENTAL METHOD

The experimental apparatus used in these studies of the neon-copper hollow cathode discharge was the same as that described previously in the studies of helium-copper discharge.[8] The experiment was performed using a cylindrical Pyrex tube with quartz end windows. This tube was part of a standard high-vacuum system which had a background pressure of 10^{-9} Torr after bakeout at 350°C for 24 h. Research-grade neon gas in 1-l Pyrex flasks was used after further purification by the cataphoretic segregation process. Final impurity levels in the neon gas were estimated to be less than 1 part per 10 million.

The reader is referred to the previous studies[8] for a detailed description of the discharge tube. The main discharge region consisted of a cylindrical copper cathode 15 cm long and 1.1 cm in diameter which had a 2-mm-wide axial slit into which was inserted the knife edge of a stainless-steel anode. This discharge configuration had a characteristic diffusion length $\Lambda=0.23$ cm. The main discharge was produced by pulsed dc voltages of 300—500 V with pulse widths of 0.4—1.0 msec and currents of 10 mA to 2 A. An auxiliary wire electrode was placed outside one end of the slit in the copper cathode and a 0.2-mA dc discharge was maintained between it and the cathode to achieve reliable breakdown for each voltage pulse.

Standard absorption techniques were used to measure the number density of ground-state copper atoms and metastable neon atoms.[10,11] A capillary discharge tube containing 2.5 Torr of neon was used as a light source for absorption measurements of $Ne^m(^3P_2)$. The light source tube for absorption studies on $Cu(4s\ ^2S_{1/2})$ consisted of a cylindrical copper hollow cathode, a wire anode, and a quartz window. This light source tube contained 5 Torr of neon. dc voltages of 300—400 V with currents of 20—30 mA were used for each light source.

The 594.5-, 614.3-, and 633.4-nm neon lines were used for absorption studies on $Ne^m(^3P_2)$ and the 324.8- and 327.4-nm Cu I resonance lines were used for absorption studies on $Cu(4s\ ^2S_{1/2})$. A Jarrel-Ash 0.5-m Ebert monochromator and a thermoelectrically cooled EMI Gencom Inc. (S-20) photomultiplier were used to analyze and detect these spectral lines. The signal from the photomultiplier was directly counted and stored in a computer controlled multichannel scaling system.

III. DATA ANALYSIS

During the application of the pulsed dc power, the ground-state copper atoms are produced by sputtering at the cathode. At the end of the pulse, the Cu density profile decays close to the fundamental diffusion mode within a few hundred microseconds into the afterglow. During the afterglow, ground-state copper atoms, $Cu(4s\ ^2S_{1/2})$, are lost by diffusion to the walls and by the reactions (3)—(5). No significant production of $Cu(4s\ ^2S_{1/2})$ by electron-ion recombination occurs during the afterglow period. However, under the experimental conditions used, the loss of $Cu(4s\ ^2S_{1/2})$ by reactions (3)—(5) can be neglected. This was confirmed by later measurements. Therefore, the continuity equation for $Cu(4s\ ^2S_{1/2})$ is just a simple diffusion equation and the solution is, in the late afterglow, a single exponential function, since only the fundamental decay mode is significant in the later afterglow. As a result, the time dependence of the ground-state copper density is given by

$$n_{Cu}(t)=n_{Cu}(0)e^{-t/\tau}, \tag{6}$$

with

$$\frac{1}{\tau}=\frac{D}{\Lambda^2}, \tag{7}$$

where D is the diffusion coefficient of $Cu(4s\ ^2S_{1/2})$ in neon. Thus the diffusion coefficient can be determined by measuring the late afterglow decay time constant using optical-absorption techniques.

Many studies[11—13] have been done concerning the time dependencies of the densities of active neon species in pure neon afterglows. However, in the Ne-Cu system described here, various active neon species decay faster than in pure neon due to extra loss processes. When copper is sputtered from a cathode surface it is ejected not only as single atoms but also as clusters of two or more atoms.[14,15] These clusters can act as efficient deexcitation centers for the active neon species and significantly alter their decay rates. The effects of these additional loss processes have to be considered when analyzing the data.

The light intensity $I(t)$ for lines originating from the various copper-ion excited states is directly proportional to the production rate of these states. This is because the radiative lifetimes of these Cu II states are several orders of magnitude smaller than the typical afterglow time constant. If a particular Cu II state is produced by one of the reactions (3)—(5), either directly or by cascading, the intensity of a line originating from this level is given by

$$I_m(t)\propto n_i(t)n_{Cu}(t)\left[k_{im}+\sum_{j\,(>m)}\alpha_{jm}k_{ij}\right], \tag{8}$$

where m and j denote particular Cu II excited states ($m=1$ for the Cu II ground state and m increases by one for successively higher Cu II energy levels), $n_i(t)$ is the time-dependent density of the particular active neon species [$i=1$ for Ne^+, $i=2$ for Ne_2^+, and $i=3$ for $Ne^m(^3P_2)$] involved in the production, k_{ij} is the reaction coefficient associated with the active neon species denoted by i and the Cu II state denoted by j, and α_{jm} is the transition probability from the Cu II level denoted by j to the Cu II level denoted by m. If a state is produced by two or more reactions, $I_m(t)$ is given by

$$I_m(t)\propto\sum_i n_i(t)n_{Cu}(t)\left[k_{im}+\sum_{j\,(>m)}\alpha_{jm}k_{ij}\right]. \tag{9}$$

However, the late afterglow decay of $I_m(t)$ will only be

determined by the density $n_i(t)$ of the slowest decaying active species involved in the excited-state production and is, therefore, given by Eq. (8). Thus, if a state is produced by two different reactions, and since the terms inside the parentheses of Eq. (9) are constant, $I_m(t)$ will be a combination of two exponential functions and undergo a transition at some time into the afterglow between the regime where the faster decaying neon species dominates and the regime where the slower decaying neon species dominates.

Taking the logarithm of both sides of Eq. (8), it follows that

$$\log\left[\frac{I_m(t)}{n_{\mathrm{Cu}}(t)}\right]=\log[n_i(t)]+\text{const}\ . \tag{10}$$

Therefore, a graph of Eq. (10) for various times into the late afterglow should be linear with a slope of 1 when the correct active neon species density $n_i(t)$ is used. For this method of data analysis, only relative values of $I_m(t)$, $n_{\mathrm{Cu}}(t)$, and $n_i(t)$ are required. Relative values of $I_m(t)$, $n_{\mathrm{Cu}}(t)$, and $n_{\mathrm{Ne}^m}(t)$ can be measured using light-emission and -absorption spectroscopy. There is no direct way to measure the time-dependent densities of Ne^+ and Ne_2^+ by optical means. However, the time dependence of the $n_{\mathrm{Ne}^+}(t)$ and $n_{\mathrm{Ne}_2^+}(t)$ densities can be inferred using optical techniques under limited experimental conditions.[16]

For neon pressures above 10 Torr and for sufficiently small ground-state Cu densities, it can be assumed that the dominant ion in the late afterglow is Ne_2^+ and thus, by charge neutrality, that the density of the electrons is approximately equal to that of Ne_2^+. This is a reasonable assumption, since in this pressure range the number density of Ne^+ decays very fast. Then the time dependence of the light-emission intensity of the neon 585.2-nm line which originates from the $3p$ level of neon is proportional to the square of the Ne_2^+ density since the $3p$ level of neon is dominantly produced in the late afterglow by the dissociative recombination process

$$\mathrm{Ne}_2^+ + e \rightarrow \mathrm{Ne}^*(3p) + \mathrm{Ne}\ . \tag{11}$$

Thus, a plot of Eq. (10) using $n_i(t)=I_{\mathrm{Ne},\ 585.2\,\mathrm{nm}}(t)$ should be linear with a slope of $\frac{1}{2}$ for those Cu II states produced by reaction (4). For very low neon pressures and for sufficiently small ground-state Cu densities, it can be assumed that the dominant ion in the late afterglow is Ne^+ and thus, by charge neutrality, that the density of electrons is approximately equal to that of Ne^+. If this assumption is valid, the time dependence of the light-emission intensity of the neon 574.8-nm line which originates from the $4d$ level of neon is proportional to the cube of Ne^+ since the $4d$ level of neon is dominantly produced in the late afterglow by the three-body recombination process

$$\mathrm{Ne}^+ + 2e \rightarrow \mathrm{Ne}^*(4d) + e\ . \tag{12}$$

Thus a plot of Eq. (10) using $n_i(t)=I_{\mathrm{Ne},\ 574.8\,\mathrm{nm}}(t)$ should be linear with a slope of $\frac{1}{3}$ for those Cu II states produced by reaction (3). The validity of these assumptions will be discussed in more detail in the next section.

IV. RESULTS AND DISCUSSION

The time dependence of the ground-state Cu($4s\ ^2S_{1/2}$) density was first investigated for neon pressures from 2 to 15 Torr and for pulsed discharge currents of 40 mA to 2 A with maximum duty cycles of 0.05. The Cu($4s\ ^2S_{1/2}$) density was measured from fractional absorption of the 324.8- and 327.4-nm Cu resonance lines. The decay of the Cu density became exponential about 0.5 msec after the end of the discharge pulse. The absolute density of Cu at the center of the discharge region during the first part of the decay was on the order of 10^{10}–10^{11} atoms/cm^3, which is sufficient for the experiments. The largest value of the absolute density of Cu obtained in these studies was 5.2×10^{11} atoms/cm^3 with a discharge current of 2 A, a pulse width of 400 μsec, and a neon pressure of 2 Torr. The measured values of P_0/τ for the Cu($4s\ ^2S_{1/2}$) decays are plotted as a function of P_0 in Fig. 2. The resulting best fit to the data gives a diffusion coefficient of $DP_0=220\pm8$ cm^{2}sec^{-1}Torr. Independence of P_0/τ on P_0 as seen in Fig. 2 indicates that the loss of Cu by reactions (3)–(5) is much smaller than the loss of Cu by diffusion.[17]

The afterglow spectrum of the Ne-Cu discharge was scanned from 200 to 800 nm at several different pressures in order to determine which transitions were present. The spectrum consisted of Cu I, Cu II, and Ne I lines. Of the Cu II spectral lines[18] observed, 37 were of sufficient intensity to be used in the study of the decay rates of various Cu II energy levels. These lines originated from 16 Cu II energy levels between the energies of 15.96 and 21.41 eV. These are listed in Table I. The notation of Moore[19] has been used to identify the Cu II levels. It was found that these levels could be divided into three groups, with levels in the same group having the same time dependence in the late afterglow. Group 1 consists of three Cu II energy levels with energies between 21.16 and 21.41 eV. Group 2 consists of one Cu II energy level with an energy of 19.58 eV. Group 3 consists of twelve Cu II energy levels with energies between 15.96 and 21.12 eV. Radiation from the Cu II levels whose energies are higher than 21.6 eV, the energy of Ne^+, was not observed.

Figures 3 and 4 show representative decays for each

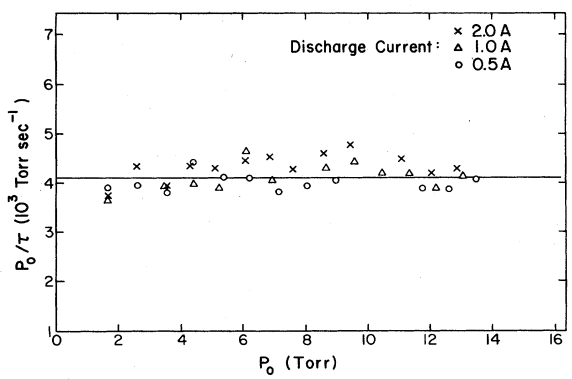

FIG. 2. Measured values of p_0/τ for Cu($4s\ ^2S_{1/2}$) as a function of p_0 with a discharge current of (○) 0.5 A, (△) 1 A, and (×) 2 A.

TABLE I. The 16 Cu II levels monitored during the Ne-Cu afterglow grouped according to the time dependence of their emission intensities.

Group 1	
Level	Energy (eV)
$5s\,^3D_2$	21.16
$^3D_1$	21.38
$^1D_2$	21.41
Group 2	
Level	Energy (eV)
$4s^2\,^1G_4$	19.58
Group 3	
Level	Energy (eV)
$4p\,^3P_2$	15.96
$^3P_1$	16.15
$^3F_3$	16.21
$^3F_4$	16.25
$^3F_2$	16.39
$^3D_3$	16.51
$^3D_2$	16.59
$^1F_3$	16.64
$^3D_1$	16.79
$^1D_2$	16.82
$^1P_1$	16.85
$5s\,^3D_3$	21.12

group for two different neon pressures. For neon pressures lower than 8 Torr, as can be seen from Fig. 3, the final decay rates of the population density of the levels in groups 1 and 3 are identical but are faster than the final decay rate of the population density of the level in group 2. This indicates that two separate reaction mechanisms are responsible for the production of the Cu II levels in groups 1 and 3 and group 2. As the neon pressure was increased, the time dependence of the decay curves in group 3 started to deviate from that of the decay curves in group

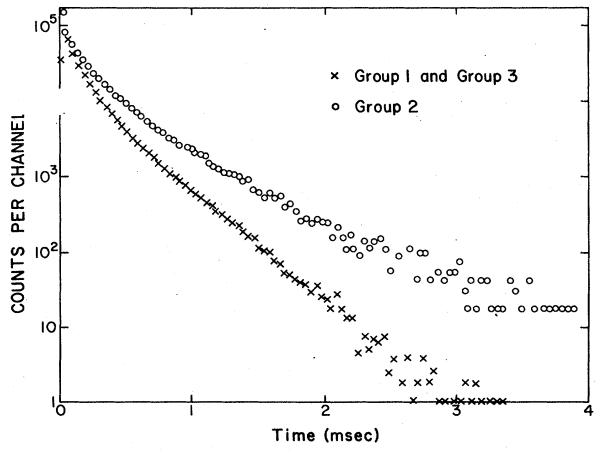

FIG. 3. Time dependencies of the line-emission intensities of Cu II levels in (×) group 1 and group 3 and (○) group 2 for a pressure of 4 Torr and a discharge current of 1 A.

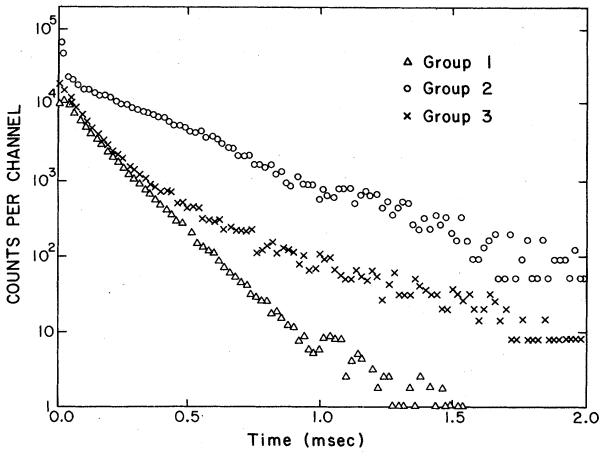

FIG. 4. Time dependencies of the line-emission intensities of Cu II levels in (△) group 1, (○) group 2, and (×) group 3 for a pressure of 14 Torr and a discharge current of 1 A.

1. This happened for a neon pressure around 10 Torr. For neon pressures above 10 Torr, the decay curves of the Cu II levels in group 3 are a combination of two exponentials. This indicates that the Cu II levels in group 3 are produced by two different reactions, either directly or by cascading.

Group 2 consists of only one Cu II level whose energy is about 0.8 eV below Ne_2^+. The time dependence of the spectral intensity from this level is well fitted to a single exponential for the entire pressure range studied. A graph of $I(t)/n_{Cu}(t)$ vs $I_{Ne,\,585.2\,nm}(t)$ is plotted on a double logarithmic scale in Fig. 5 for the spectral intensity $I(t)$ coming from this level and for a neon pressure of 12 Torr and a discharge current of 1 A. Figure 5 shows that this plot is linear with a slope of $\frac{1}{2}$. Thus it can be concluded that the Cu II level, $4s^2\,^1G_4$, is populated by reaction (4). In addition, the single exponential decay indicates that the production of this level by reaction (3), either directly or by cascading, is negligible under the current experimental conditions.

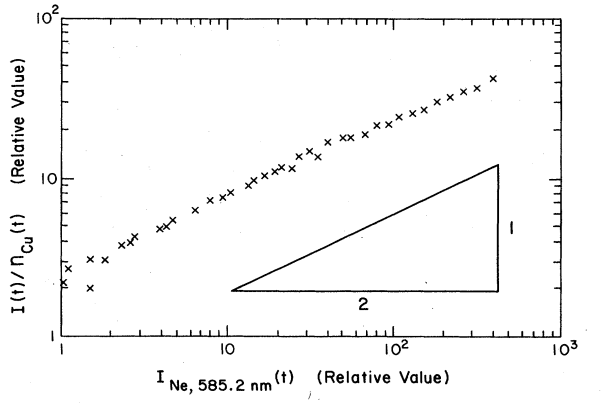

FIG. 5. Graph of relation (10) for the emission intensity of the 404.3-nm Cu II line from the $4s^2\,^1G_4$ level in group 2 and for the emission intensity of the Ne 585.2-nm line during the afterglow period for a pressure of 12 Torr and a discharge current of 1 A. Each data point corresponds to the values of the relative intensities and density at a given time into the afterglow.

In order to determine the experimental conditions over which the assumption that Ne_2^+ is the dominant ion holds, the graphs of $I(t)/n_{Cu}(t)$ vs $I_{Ne,\,585.2\,nm}(t)$ on a double logarithmic scale, with the spectral intensity $I(t)$ coming from the level in group 2, were plotted for several different neon pressures and different discharge currents. At a discharge current of 0.5 A, the slopes of the plots are $\frac{1}{2}$ from 15 Torr down to 5 Torr. The slopes then tend to increase as the pressure goes below 5 Torr. This indicates, at the discharge current of 0.5 A, that the above assumption is valid for neon pressures of 5 to 15 Torr but that Ne_2^+ is no longer the dominant ion below 5 Torr. At a discharge current of 1 A, the slopes are $\frac{1}{2}$ from 15 to 12 Torr and then tend to increase as the pressure goes below 12 Torr. At a discharge current of 2 A, the slopes are always larger than $\frac{1}{2}$ and this indicates that Ne_2^+ is no longer the dominant ion over any of the pressure range studied. The dependence on the discharge current of the cutoff pressure above which the assumption is valid is consistent with the fact that as the pressure is decreased with constant current or as the discharge current is increased with the same pressure, the sputtering rate is increased and, therefore, the absolute number density of $Cu(4s\,^2S_{1/2})$ and, hence, of Cu^+ is also increased. Comparing the measured values of the initial densities of Cu atoms with the slopes of the graphs of Eq. (10) for Ne_2^+, it was found that the assumption that Ne_2^+ is the dominant ion is safe whenever the initial Cu atom density is less than 4×10^{10} cm^{-3}. Above this initial Cu atom density limit, the Cu^+ density must become comparable to or larger than the Ne_2^+ density.

The energies of the Cu II levels in group 1 are between the energies of Ne^+ and Ne_2^+. All these levels are probably produced, either directly or by cascading, by the charge-transfer reaction (3). This is because Ne^+ is the only active neon species which has enough energy to produce these Cu II levels. This mechanism could not be confirmed directly, however, since the necessary condition that Ne^+ be the dominant ion at low neon pressures could not be satisfied. When the graphs of $I(t)/n_{Cu}(t)$ vs $I_{Ne,\,574.8\,nm}(t)$ were plotted on a double logarithmic scale with the spectral intensity from the levels in group 1, the slopes are always larger than $\frac{1}{3}$ for all experimental conditions studied. Thus the assumption that Ne^+ is the dominant ion at low pressures is apparently not valid under these experimental conditions, since the Cu^+ density is always comparable to or larger than the Ne^+ density in this pressure region.

The Cu II levels in group 3 have energies between 21.12 and 15.96 eV and are all energetically accessible, either directly or by cascading, for energy transfer from the lowest vibrational level of ground state Ne_2^+ except for one level, $5s\,^3D_3$, whose energy is 0.9 eV above the lowest vibrational level of Ne_2^+. It should also be noted that the energy of $Ne^m(^3P_2)$ is between the energies of the $4p\,^3D_2$ and $4p\,^1F_3$ levels of Cu II. In the pressure range from 2 to 8 Torr, the decay shapes of spectral lines originating from the levels in group 3 are identical to those from the levels in group 1. Therefore, in this pressure range, these levels are predominantly produced only by reaction (3), by cascading from higher energy levels. As the neon pressure is increased above 8 Torr, these decay curves undergo a transition and have the final decay shapes as indicated in Fig. 4. In order to determine which reaction is responsible for this transition, $I(t)/n_{Cu}(t)$ vs $n_{Ne^m}(t)$ is plotted on a double logarithmic scale for the Cu II 213.5-nm line originating from the $4p\,^3F_4$ level whose energy is 0.35 eV below $Ne^m(^3P_2)$. The resulting slope, after the transition point, is definitely unequal to 1. In addition, since the measured value of the $Ne^m(^3P_2)$ density decay rate is slower than that of the Ne_2^+ density decay rate for the pressure range studied, a slower late afterglow decay rate should be observed for the group-3 levels below 16.6 eV than for the levels above 16.6 eV if reaction (5) is of importance. However, this was not the case. Therefore, none of the Cu II levels in group 3 are predominantly produced by $Ne^m(^3P_2)$. The final decay rate of the spectral intensity from these levels for pressures above 8 Torr is identical, however, to the decay rate of the $4s^2\,^1G_4$ level in group 2. Thus it can be concluded that the Cu II levels in group 3 are predominantly produced at low pressures (less than 8 Torr) by Ne^+ through reaction (3) and subsequent cascading and at pressures higher than 8 Torr by the two separate reactions (3) and (4).

According to Table I, the Cu II $5s\,^3D_3$ level, whose energy is 21.12 eV, is included in group 3. The spectral intensity originating from this level behaves the same way as the rest of the levels in group 3, even though this level is not energetically accessible to the lowest vibrational level of Ne_2^+. Fortunately there is good evidence[20] that an appreciable density of vibrationally excited Ne_2^+ levels can exist during the afterglow of a pure neon discharge. From the calculated energy values of the vibrational levels of Ne_2^+,[21] the 17th excited vibrational level is needed to have enough energy to produce the Cu II $5s\,^3D_3$ level by reaction (4). This also explains why the decay curves of this level undergo a transition from the fast-decaying regime to the slow-decaying regime at a higher pressure and later time into the afterglow than that of the other levels in group 3. For example, the decay curve for Cu II $5s\,^3D_3$ underwent the transition after about 0.8 msec into the afterglow, while the decay curve of Cu II $4p\,^1P_1$ underwent the transition after about 0.4 msec into the afterglow for studies at a pressure of 14 Torr and a discharge current of 1 A. This is due to the fact that the absolute number density of the vibrationally excited state of Ne_2^+ is much smaller than the absolute number density of the vibrationally relaxed state of Ne_2^+.

It is also worthwhile to note that no spectral lines from the Cu II levels $4s^2\,^1D_1$, $4s^2\,^3P_2$, $4s^2\,^3P_1$, and $4s^2\,^3P_0$, whose energies are between 18.31 and 18.75 eV, were observed. These four Cu II levels would appear to be good candidates for reaction (4), with energy defects ranging from 1.46 to 1.9 eV. A possible explanation for the lack of reactions involving these Cu II levels can be given by assuming that the reaction proceeds as

$$Ne_2^+ + Cu \rightarrow (Cu^+)^* + (Ne_2)_r \longrightarrow 2Ne\,, \qquad (13)$$

where $(Ne_2)_r$ is the molecular neon repulsive ground state. The available energy for the excitation of Cu II levels by Ne_2^+ via process (13) can be calculated. From the potential energy curves[22–24] for Ne_2^+ and $(Ne_2)_r$, the available energy range is from 18.67 to 19.29 eV, assuming Frank-Condon transitions. The energies of the four Cu II levels between 18.31 and 18.75 eV are right on the edge of the available energy range, and this could be the reason why the production of these Cu II levels by reaction (4) is negligible.

V. CONCLUSION

The time dependencies of the spectral intensities originating from various Cu II levels were studied in the stationary afterglow of the Ne-Cu discharge. The time dependencies of the number densities of $Cu(4s\ ^2S_{1/2})$ and $Ne^m(^3P_2)$ were also measured using standard absorption techniques. From these measurements the diffusion coefficient of $Cu(4s\ ^2S_{1/2})$ in neon was determined to be $DP_0 = 220 \pm 8\ cm^2\ sec^{-1}\ Torr$.

The spectral intensities of 37 lines originating from 16 Cu II levels were studied. These levels could be divided into three groups according to their final decay rates. The three levels in group 1 are predominantly produced by charge-transfer with Ne^+ and the one level in group 2 is predominantly produced by charge transfer with Ne_2^+, for all the neon pressures studied. The twelve levels in group 3, whose energies range from 15.96 to 16.85 eV, are predominantly produced by charge transfer with Ne^+ and subsequent cascading at neon pressures below 8 Torr and are produced by both Ne^+ and Ne_2^+ at neon pressures above 8 Torr. The $5s\ ^3D_3$ level in group 3, whose energy is 21.12 eV, is predominantly produced by charge transfer with Ne^+ at neon pressures below 10 Torr and is produced by both Ne^+ and Ne_2^+ at neon pressures above 10 Torr. No evidence was found for the production of Cu II excited states by the Penning ionization of Cu by $Ne^m(^3P_2)$.

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