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Cross Sections for Collisions of the Second Kind in a Helium-Neon Discharge

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The collisional transfer of energy between two excited states in a gas discharge may be described by a two-body inelastic cross section. The energy dependence of the two-body cross section for collisions of the second kind between the He 2^1S metastable and Ne $3s_2$ states has been investigated. This process is primarily responsible for populating the upper level of the 6328-Å laser transition. Pulsed afterglow measurements were performed as a function of gas temperature and pressure. The experiments were conducted at low gas temperatures so that the effect of energy transfer from the helium metastable level to other nearby neon levels could be minimized. The measured decay rates departed substantially from that predicted by using an energy-independent cross section. A unit-step cross section for the He 2^1S-Ne $3s_2$ resonant transfer process with a value of $(1.0\pm0.15)\times10^{-15}$ cm^2 and with a threshold energy corresponding to the energy difference between the two levels was determined.

I. INTRODUCTION

The discrete character of energy levels in a gas discharge requires that an inelastic collision between an excited atom and a normal atom, resulting in a transition to a higher excited state, be accompanied by the exchange of a certain minimum threshold energy. For collisions of the second kind, involving energy transfer from excited states of one species to those of another species by collisions with ground-state atoms, this minimum threshold energy corresponds to the energy difference between the two excited levels. The energy for the process is supplied by a change in the kinetic energy of the atoms. When collisions are the primary mechanism for kinetic-energy exchange among the atoms, their motion may be described by a Maxwellian energy distribution at a specific gas temperature.

The usual way of characterizing two-body gas collisions is to define a velocity-averaged cross section at a particular temperature, which is energy independent. This cross section is normally used to describe energy transfer between energy levels which are within a few kT of each other. Since the actual cross section must have a minimum threshold energy, any attempt to use such a cross section over a wide range of gas temperatures can result in serious errors. The interaction is often further complicated at higher temperatures by the presence of inelastic transfer to other nearby ener-

gy levels, as well as to the level under consideration.

At gas temperatures which are sufficiently low, very few atoms can exchange the minimum kinetic energy necessary for excited-state transfer to any but the closest of nearby energy levels. In principle, considerable changes in the rate of inelastic collisions should then be present at higher temperatures, where transfer to many excited states becomes significant.

The present experiment is concerned with the determination of the energy-dependent cross section for resonant transfer between the He $1s2s\ ^1S_0$ level and the Ne $(2p)^5 5s\ ^1P_1$ level. This neon level is designated as the $3s_2$ level in Paschen notation and is the upper level of the 6328-Å He-Ne laser transition. A unit-step collisional cross section was determined by observing the spontaneous-emission time decay of the Ne $3s_2$ level as a function of temperature and pressure in a pulsed low-temperature afterglow experiment. The measurements were performed at low temperatures to minimize the effect of second-kind collisions between the helium metastable and nearby neon levels.

II. AFTERGLOW RELATIONS

Metastable levels have lifetimes that are normally long with respect to those of radiative levels. If a gas discharge is pulsed off and the electronic excitation decays in a time which is rapid with respect to a metastable lifetime, the metastable state may continue to populate nearby radiative levels in the afterglow by collisions of the second kind. The slow decay rate of a radiative level, populated exclusively by such a process, may then be expressed in terms of the metastable lifetime and the total cross section for deexcitation of the metastable by foreign gas collisions.

Afterglow measurements of the neon 1.15-μ transition were conducted by Javan *et al.*[1] while studying the populating mechanisms of the original 1.15-μ laser. They determined a total velocity-averaged cross section between the He 2^3S metastable level and the Ne $2s_2$ and $2s_3$ levels. Subsequently, collisions of the second kind between He 2^1S metastables and neon atoms were found to be primarily responsible for populating the Ne $3s_2$ level, the upper level of the 6328-Å laser transition.[2] Later optical-absorption afterglow experiments[3] involving He-Ne mixtures showed a strong dependence of the He 2^3S and 2^1S lifetimes on temperature. Afterglow experiments performed by others[4] indicated that the $4f$-$4d$ laser lines were also excited by collisions with the He 2^1S metastable. The neon $4f$ levels are approximately $4kT$ (800 cm^{-1}) above the helium singlet metastable level, as opposed to the neon $3s_2$ level which is approximately 400 cm^{-1} above the metastable level.

At low temperature, coupling with the $4f$ levels may be minimized, and the steady-state rate equations for the He 2^1S and Ne $3s_2$ levels may be written, respectively,[5] as

$$\frac{dN_1}{dt} = 0 = \alpha_1 N_e N_0 - \beta_1 N_e N_1 - Z_r N_1 + Z_r' N_2 - Z_d N_1 , \tag{1}$$

$$\frac{dN_2}{dt} = 0 = Z_r N_1 - Z_r' N_2 - A N_2 , \tag{2}$$

in which N_0 is the ground-state helium density, αN_e is the direct-electron-excitation rate per atom (sec^{-1}), $\beta_1 N_e$ is the electron collisional deexcitation rate per metastable, Z_r and Z_r' are the forward and reverse resonant transfer-rate coefficients, respectively, Z_d is the metastable diffusion-rate coefficient, and A refers to the sum of the inverse trapped radiative lifetime of the Ne $3s_2$ level and all other possible current-independent deexcitation mechanisms involving the Ne $3s_2$ level. At low currents where electron collisional deexcitation is negligible, the second term in Eq. (1) may be ignored. The rate at which atoms are returned to the metastable level by reverse resonant transfer $Z_r' N_2$ has been found experimentally to be small with respect to the rate at which atoms leave level one by resonant transfer collision.[6] Consequently, the fourth term in Eq. (1) may also be neglected. Alternately, this approximation implies that $Z_r' \ll A$. The partial pressures and diameter of the test cell may be chosen such that the diffusion loss of the He 2^1S level is small with respect to the resonant transfer rate. In the afterglow, the metastable state will then decay in a time inversely proportional to Z_r, provided that the direct electron excitation is removed in a time that is rapid with respect to the inverse of Z_d. Since the lifetime of the neon level is short with respect to that of the metastable state, the decay rate of the neon level may also be expected to follow that of the metastable state in the late afterglow.

The resonant transfer rate is directly proportional to neon pressure, while at large helium-neon ratios the diffusion coefficient varies inversely with helium pressure.[5] The validity of the preceding approximations may thus be established by observing the partial-pressure dependence of the time-decay measurements.

III. EXPERIMENT

The experimental apparatus is illustrated in Fig. 1. A short cold-cathode positive-column discharge tube was suspended in an insulated Dewar and connected to a mercury diffusion vacuum system capable of pumping out the tube to $\sim 10^{-7}$ Torr. The tube was filled with various He-Ne pressures and mixtures, but was typically operated at helium pressures of 1 Torr and at neon pressures of less

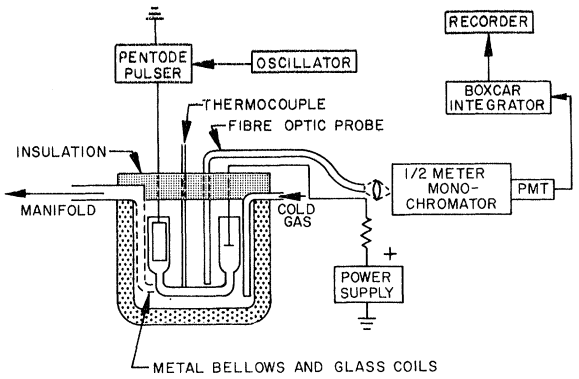

FIG. 1. Block diagram of the experimental apparatus for low-gas-temperature spontaneous-emission afterglow measurements.

than 60 μ. The positive-column discharge length was approximately 15 cm with an inside diameter of 13 mm. The discharge was pulsed on and off at a frequency of 4 kHz with an average current of 5 mA. The rise and fall time of the tube current was approximately 1 μsec. The current was chosen to be relatively small in order to avoid complicating considerations introduced by electron collisional deexcitation processes and in order to achieve the lowest possible temperatures with the available cooling power. The Dewar was cooled by flowing cold nitrogen gas from a large liquid-nitrogen reservoir into the system. The temperature of the Dewar and discharge-tube assembly were controlled by adjusting the flow rate of the cold nitrogen gas. Temperatures as low as 150 °K could be achieved. In order to maintain gradual temperature gradients between the large gas reservoir at the vacuum station and the cooled tube, the external gas was forced to pass through a coiled section of glass, immersed in the Dewar, before entering the discharge tube. Metal bellows were connected to either end of the coiled section to facilitate thermal contact between the flowing nitrogen and the helium.

The temperature in the discharge region was determined from an iron-constantan thermocouple sealed directly into the positive column. External thermocouples were placed at various locations in the cooled assembly to provide auxiliary readings. A fiber-optic light guide was positioned a few centimeters from the discharge thermocouple in order to avoid the perturbing effect of the thermocouple. The far end of the flexible fiber-optic probe was imaged onto the entrance slit of a monochromator. The photomultiplier output was then passed through a 1-MHz preamplifier into a boxcar integrator where the afterglow decay rates were extracted.

The electron-afterglow decay time was observed by monitoring the decay rates of the He 4^1D-2^1P (4922-Å) line, which was found to be characteristic of the decay rate of spectral lines originating from other D levels. These lines showed a linear current dependence indicative of direct electron excitation. The decay time of the 4922-Å line was determined to be less than 4 μsec. Since the natural lifetimes of the D lines are in the submicrosecond range, the observed decay time could be taken as a measure of the decay of the electron-afterglow excitation rate.

For typical pressure and temperature ranges, the time decay of the 6328-Å spontaneous emission varied from 10 to 30 μsec. In order to minimize the effect of electron-afterglow transients on the decay rates of the He 2^1S or the Ne $3s_2$ levels, the spontaneous-emission decay measurements were delayed until 20 μsec after the tube current had been pulsed off. It was necessary to vary both the He and Ne pressures to verify that collisions of the second kind were indeed the dominant decay mechanism for the He 2^1S metastable level. At constant neon pressure and temperature, the measured decay rates did not vary with helium pressure over the range 0.6–1.5 Torr. At constant helium pressure and temperature, the decay rates were found to vary inversely with neon pressure. This indicated that neon collisions (i.e., the rate coefficient Z_r) were indeed the primary mechanism for destruction of the metastable states.

Observations of spontaneous-emission magnitudes showed that the excitation rate from the metastable to the slightly more coincident neon $3s_3$ level was relatively small, in agreement with results from previous experiments.[7] At low temperatures, the nearest interacting level with the helium metastable was then considered to be the neon $3s_2$ level.

IV. RESULTS AND ANALYSIS

The resonant transfer rate from the helium metastable to the neon $3s_2$ level may be expressed as

$$Z_r = N_{\mathrm{Ne}} \int_0^\infty \sigma(v)\, v f(v)\, dv \,, \tag{3}$$

where N_{Ne} is the ground-state neon density, $f(v)$ is the normalized Maxwellian atomic-velocity distribution, v is the atomic velocity, and $f(v)$ is the velocity- or energy-dependent cross section. If the cross section is assumed to be energy independent and if the atomic kinetic energy is large compared with the threshold energy ($kT \gg E_1$), the usual expression for velocity-averaged transfer is obtained,

$$Z_r = N_{\mathrm{Ne}}\, \sigma\, \bar{v} = N_{\mathrm{Ne}}\, \sigma\, (8kT/\pi m)^{1/2} \,, \tag{4}$$

$$m = M_1 M_2/(M_1 + M_2) \,.$$

When $\sigma(v)$ is assumed to be a unit step with a threshold energy E_1, Eq. (3) yields

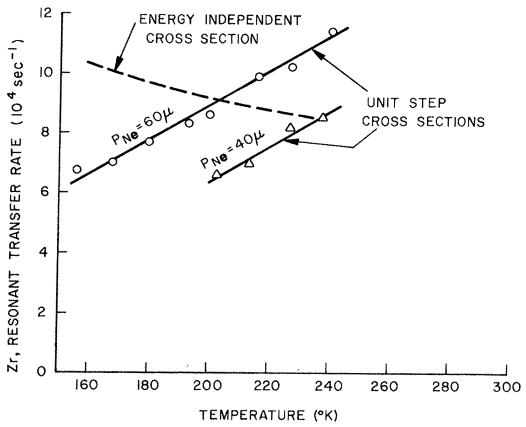

FIG. 2. Experimental results for neon pressures of 60 and 40 μ at a helium pressure of 1 Torr. Best fits to a unit-step cross section and an approximate fit to a velocity-averaged cross section are indicated.

$$Z_r = N_{Ne}\,\sigma\,(8kT/\pi m)^{1/2}\,(1 + E_1/kT)\,e^{-E_1/kT}\ . \qquad (5)$$

Equation (5) is fitted to the experimentally observed time decays in Fig. 2 to obtain a value for the unit-step resonant-transfer cross section of $(1.0 \pm 0.15)\times 10^{-15}$ cm^2. The results do not show any discontinuities that might indicate the presence of excitation transfer to other energy levels. The measurements were made at constant pressure as a function of temperature ($p = N_{Ne}\,kT$). At constant temperature, the ratios of the two sets of experimental points are within 15% of the expected 1.5:1 ratio of neon partial pressures. A crude fit to a velocity-averaged cross section for a neon partial pressure of 60 μ is also indicated in Fig. 2, from which it becomes apparent that the use of such a cross section can lead to serious errors in the estimations of resonant transfer rates.

Typical experimental resolution corresponding to the approximately 20 °K temperature increments of Fig. 2, is presented in Fig. 3. A third curve is also presented in Fig. 3, corresponding to a 33% lower neon partial pressure. In all cases only a single exponential is evident so that Z_r is simply inversely proportional to the exponential time constant.

A cross section of the form[5]

$$\sigma = \sigma_0\, 2[(E - E_1)/E_1]\, e^{-2(E-E_1)/E_1}$$

may also be chosen for comparison with the data. This cross section has a maximum value at $1.5E_1$, and approaches zero for $E \gg E_1$. In the temperature region considered, a fit of this integrated cross section to the experimental data is nearly indistinguishable from that of a unit step.

At 300 °K, the unit-step cross section of 1.0×10^{-15} cm^2 produces the same resonant-transfer rate as a velocity-averaged cross section of 4.6×10^{-16} cm^2. This value compares favorably with a velocity-averaged cross section of 4.1×10^{-16} cm^2 obtained from time-resolved optical-absorption techniques.[8]

V. CONCLUSIONS

The techniques presented here need not be restricted to metastable collisions with foreign gases in the afterglow. In principle, they can be applied on a transient or steady-state basis to any two collisionally coupled levels to extract an energy-dependent cross section. The perturbation may, for example, be optical or by electron impact. In practice, the primary restriction on the usefulness of this method for transient analysis is that one of the levels must be perturbed in a time that is short compared with the relaxation time of the level.

Over a wide range of temperatures, the use of an energy-independent cross section for describing a two-body excited-state inelastic collision process can lead to significant errors. An afterglow technique has been presented which allows the determination of an energy-dependent collisional cross section by varying the temperature and partial pressure of the gas discharge. Undesired interactions with nearby levels were largely eliminated by reducing the temperature of the system. A unit-step

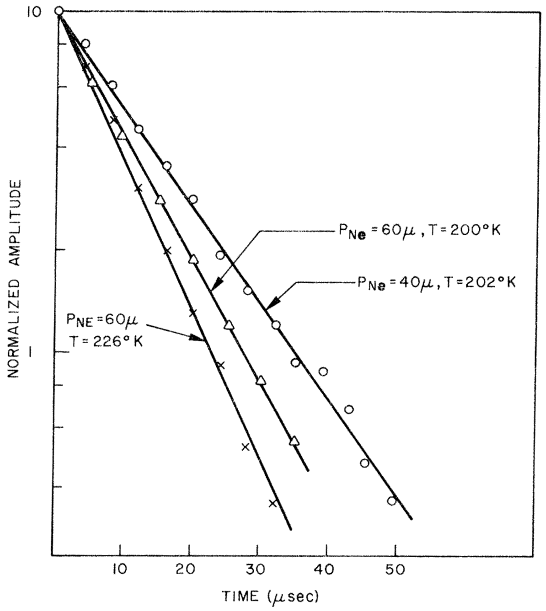

FIG. 3. Afterglow spontaneous-emission intensities for 1 Torr of helium at two temperatures and at two neon partial pressures.

cross section with a value of $\sigma_r = (1.0 \pm 0.15) \times 10^{-15}$ cm^2 was determined for the resonant-transfer collision process between the He 2^1S metastable level and the Ne $3s_2$ level.

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Two Electrons in a Coulomb Potential. Double-Continuum Wave Functions and Threshold Law for Electron-Atom Ionization*†

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The Schrödinger equation for two electrons in a Coulomb field is studied in the critical region where both electrons have near-zero kinetic energies. The main feature of this problem is that the mutual screening between the two electrons determines and is determined by the partition of the available energy between them. This energy-dependent screening can be taken into account to yield a complex potential in the radial variable $R = (r_1^2 + r_2^2)^{1/2}$ of the six-dimensional configuration space of the two electrons. Solutions of this equation are obtained and are shown to correspond to the classical orbits given in an early paper by Wannier. A possible way is indicated of using these wave functions to establish the Wannier threshold law which, for ionization of neutral atoms, is $\sigma \propto E^{1.127}$. Finally, the interplay between the total energy and the Coulomb potential is discussed both for this problem and for the case of one electron in the field of a nucleus.

I. INTRODUCTION

The increasing attention being given, in both experimental and theoretical atomic physics, to correlation effects between electrons makes the prototype system of two electrons in the field of a nucleus of increasing conceptual and practical interest. The correlation effects are expected to be especially significant when the two electrons have near-zero energies. This is a situation that obtains in the classic three-body problem of the threshold behavior of the cross section for ionization of atoms by electron impact.[1] As we will see, a crucial feature of the two-electron continuum wave functions near threshold is that they include a large number of spherical harmonics of *either* electron,[2] even when the *total* wave function is restricted to an S state. The divergence of this number distinguishes the ionization threshold from the threshold for excitation of any level that lies below the ionization limit by a finite amount. Arguments for a linear threshold law for ionization on the basis of extrapolation from excited states are invalidated by this feature, which puts the ionization threshold on a *qualitatively* different footing. The same divergence in l values is of practical interest because it represents a long-range correlation which will be important for electron-atom scattering calculations at energies approaching the ionization limit from *either* direction. The influence of this effect has already been felt in close-coupling calculations of collision processes, which agree quite well with experiment when the energy is near the $n = 2$ or 3 levels and again when the energy is appreciably above the ionization limit, but depart very significantly from experiment in the intermediate range. The two-electron wave functions derived in this paper emphasize precisely this long-range angular correlation which has so far not been included in any calculation. Analogous effects should occur, of course, near the threshold for breakup into a still larger number of particles and may be analyzed along similar lines.