estimate.

The quenching effect of an external electric field was investigated by introducing a field over a 1-cm length of beam path in front of the detector. The Stark quenching observed in rubidium is shown in Fig. 4(b). A smaller effect was observed in potassium, and none in lithium. Since the electric field mixes the metastable state with neighboring states of opposite parity, same spin, and total J differing by 0 or ± 1, one might expect a significant decrease in the lifetime of metastable atoms if the neighboring states satisfying these selection rules are shorter lived. Examples of such neighboring states are $(4p^5 5s4f)\,{}^4G_{9/2,7/2}$ in Rb and $(1s2p^2)\,{}^4P_{3/2}$ in Li. Wu and Shen have estimated that the energy separation between the $(1s2p^2)\,{}^4P_{3/2}$ and $(1s2s2p)\,{}^4P_{5/2}$ states in Li is 3.43 eV. This large separation probably accounts for the absence of an observable quenching effect at the highest field attainable in our apparatus (150 000 V/cm). In K and Rb the neighboring short-lived states are probably much closer to the metastable state.

Further experiments employing the techniques of resonance spectroscopy and magnetic deflection are necessary for complete identification of the observed states, and are in progress in our laboratory. It is also desirable to extend the work of Beutler to shorter wavelengths so that the energies of the excited-core doublet states in lithium and sodium can be determined.[10]

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VARIATIONAL THEORY OF THREE-BODY ELECTRON-ION RECOMBINATION RATES*

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The rate of three-body electron-ion recombination

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

is calculated from a classical variational theory, which has proved successful in determining atomic recombination rates in the presence of repulsive third bodies.[1] The above mechanism, in which an electron acts as a third body removing the recombination energy, is known to be important at high electron densities and low temperatures when radiative transitions are unimportant.

A classical solution may be justified only when the deBroglie wavelength is smaller than the characteristic range of the interaction. The appropriate range here is Thomson's radius,[2] $2e^2/3kT$, at which the potential energy of the recombining pair is equal to the kinetic energy, and inside which two ions have a high probability of recombining. Based on this dimension a classical

solution is valid for temperatures below about 11 000°K.

In the theory the motion of the three bodies is described by a representative point in an 18-dimensional phase space. If a "trial" surface is chosen in this hyperspace separating the free and bound states, then an upper bound to the rate may be obtained by calculating the rate at which representative points cross this surface in one direction. The surface chosen for the present calculation is defined by the condition that the relative energy of the recombining electron-ion pair be $-E_c$ with respect to the dissociation limit. It is shown schematically in Fig. 1 along with a diagram of the three-particle system. The rate at which representative points cross the "trial" surface is[1]

$$R=\int\rho_0 e^{-H/kT}\vec{v}\cdot\vec{n}\,d\sigma, \qquad (1)$$

where $\vec{v}\cdot\vec{n}$ is the normal velocity with respect to an element of "trial" surface $d\sigma$, H is the total Hamiltonian, and ρ_0 is a constant. In the center-of-mass system, the flux integral is 11-dimensional and the integration may be carried out keeping

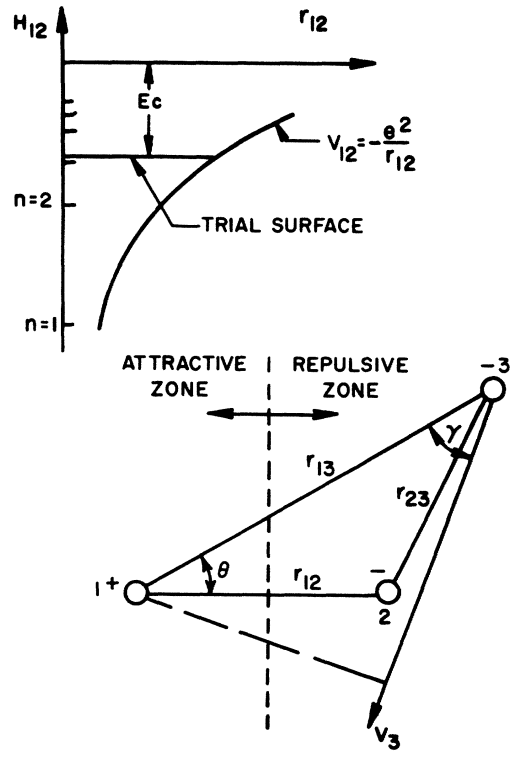

FIG. 1. Schematic diagram showing location of "trial" surface separating "free" and "bound" states of an electron-ion pair and geometry of the three-body collision.

$\epsilon_c=E_c/kT$ as an undetermined parameter. Coulomb potential fields are assumed between each pair of particles, and the three-body potential is assumed to be the sum of two-body potentials. An upper bound to the three-body recombination rate is then

$$R=n_i n_e^2 2\pi^{3/2}(8kT/\pi m)^{1/2} r_T^5 \exp(\epsilon_c)\Gamma(\epsilon_c), \qquad (2)$$

where

$$\Gamma(\epsilon_c)=\int e^{-\epsilon_3-\mu_3\frac{1}{\rho_{23}^2}\left(\frac{1}{\rho_{12}}-\epsilon_c\right)} \times\epsilon_3^{1/2}d\epsilon_3\rho_{12}^2 d\rho_{12}\rho_{13}^2 d\rho_{13}\,d\cos\theta\,d\cos\gamma \qquad (3)$$

and $r_T=e^2/kT$, $\rho_{13}=r_{13}/r_T$, $\rho_{23}=r_{23}/r_T$, $\rho_{12}=r_{12}/r_T$, $\epsilon_3=mv_3^2/2kT$, v_3 is the velocity of particle 3, and $u_3=1/\rho_{23}-1/\rho_{13}$ is the sum of the potentials between particle pairs 1-3 and 2-3 divided by kT. Other symbols are defined in Fig. 1. The integration of Eq. (3) is to be carried out subject to the conditions $\vec{v}\cdot\vec{n}\geq 0$, $H_{12}=-E_c$, and $H_{13}\geq -E_c$, where H_{12} and H_{13} are the relative energies of the two electrons with respect to the ion. The last condition is imposed to insure that one electron has not already crossed the "trial" surface and hence recombined with the ion.

As it stands, the integral in Eq. (3) diverges linearly in ρ_{13}. Such divergences are well known with Coulomb potentials and are the result of many long-range "soft" collisions. The "trial" surface may be crossed many times by a single point during such collisions resulting in a gross overestimate of the net recombination rate. However, in collisions of this type, no energy is transferred between the particles and recombination will not occur. Bohr[3] showed that when the product of the collision time τ and the angular frequency of a bound electron around its parent nucleus ω is greater than unity, the collision is adiabatic and no energy will be transferred. Since we are only interested in those collisions where energy is transferred, we may limit the integral in Eq. (3) to the region where $\omega\tau\leq 1$. The integration may then be carried out approximately[4] and the result expressed in the form

$$\Gamma(\epsilon_c)=(3/64\sqrt{\pi})[8\exp(\tfrac{3}{5}\epsilon_c)+1]\epsilon_c^{-4}. \qquad (4)$$

Equation (4) may now be minimized with respect to ϵ_c to obtain a least upper bound for the recombination rate. When $\epsilon_c=5/2$, the rate expression has a minimum value such that

$$R=2.3\times10^{-8}T^{-9/2}n_i n_e^2. \qquad (5)$$

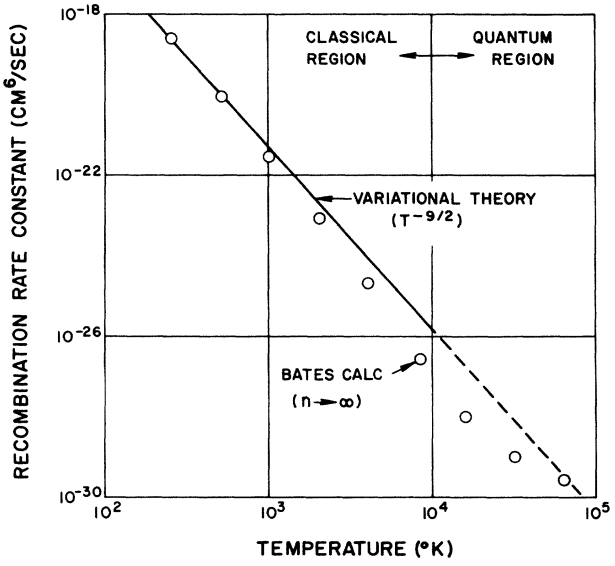

FIG. 2. Comparison of present results with those calculated by Bates for infinite electron density using Gryzinski's classical transition probabilities. Note that the extension of either Bates' or the present results into the quantum mechanical region is of doubtful validity.

The rate constant $k = R/n_i n_e^2$ obtained from Eq. (5) is shown plotted in Fig. 2 in comparison with the calculations of Bates, Kingston, and McWhirter[5] for the case in which collisional de-excitation is the dominant mechanism. Bates has considered the problem from the point of view of cascading between levels using transition probabilities obtained by Gryzinski[6] from a classical treatment of an equivalent two-body problem.

A physical explanation of the minimum, or "bottleneck," in the rate has been previously given by Byron, Stabler, and Bortz[7] whose calculations are also based on Gryzinski's transition probabilities and agree with Bates. It is the result of a decreasing equilibrium density $\exp(\epsilon_c)$ as the principal quantum number increases, combined with an increasing probability of collisional de-excitation $\Gamma(\epsilon_c)$. In the phase-space calculation both of these effects have been automatically included in the rate expression.

The existence of the "bottleneck" has been verified experimentally by Hinnov and Hirschberg.[8] They measured the population of states in a recombining helium plasma and noticed that at a depth of $(5/2)kT$ from the continuum, the population density began to fall off sharply from a value in equilibrium with the free electrons.

An important effect taken into account in the present calculation which is neglected in Gryzinski's work is the influence of the ionic charge on the motion of the "third-body" electron. The magnitude of this effect may be judged from the fact that at the "bottleneck" over 80% of the calculated recombination rate comes from the region in which the net interaction with the "third-body" electron is attractive. A further improvement is in the treatment of "adiabatic" collisions which Gryzinski eliminated by an arbitrary averaging procedure.

In concluding we should like to point out that although the theory presented here does not give results which are startlingly different from those of Bates and Byron, they were obtained in a somewhat simpler and more direct manner which is capable of giving an insight into the specifically three-body effects and can be subject to systematic improvement.

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