# Plasma Shielding Effects on Ionic Recombination

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Monte Carlo calculations are presented of the ion-ion recombination rate coefficient for the $Kr^+ + F^- + Ar$ reaction. The effect of other ions on the recombination rate is taken into account by use of the Debye screened potential rather than the Coulomb potential. This potential should be valid for ion densities between $10^{13}$ and $10^{15}$ $cm^{-3}$. Results are presented for ion densities in this range and for neutral pressures of 0.5 to 8.0 atm. It is found that screening effects significantly decrease the ion-ion recombination rate.

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Interest in the theory of ion-ion recombination has increased recently because of the development of excimer lasers. In electron-beam-pumped, rare-gas-halide, and metal-vapor-halide lasers, for example, recombination of positive rare gas or metal ions and negative halogen ions is primarily responsible for the formation of the upper laser state.[1] Until recently, experiments involving ion-ion recombination were performed in a low-plasma-density regime. In lasers, however, electron and ion densities may easily exceed $10^{13}$ $cm^{-3}$ and may even exceed $10^{15}$ $cm^{-3}$ in some high-power lasers. In such plasmas the screening of the Coulomb potential between ions by other ions and by electrons may be significant. Screening should have the effect of slowing down the recombination rate and, hence, the formation rate of the product species. Previous analytical theories[2-4] and numerical calculations[5,6] of ion-ion recombination have not included screening effects. In this Letter we present results of Monte Carlo calculations for the reaction

$$Kr^+ + F^- + Ar \rightarrow KrF^* + Ar$$

as a function of pressure and ion density using the Debye-Huckel screened potential. We discuss the limitations of this model and other, more accurate, approaches to the problem.

The $Kr^+$-$F^-$-Ar system is of obvious interest for the development of lasers. In addition, the simple nature of the potential curves and the absence of alternative channels make this a good model system for the theoretical study of ionic recombination. Mutual neutralization is likely to be a small effect ($k \simeq 10^{-9}$ $cm^3$ $s^{-1}$),[7] since the curve crossing occurs at 21 Å.[1] Because the ionic species lie lower in energy than the excited states of the neutral third body, energy loss occurs only through elastic collisions.

The theory of ion-ion recombination in low-density gases was first developed by Thomson[8] and the high-density limit was found by Langevin[9] using mobility theory. Since then there have been efforts by various authors, notably Natanson,[10] Bates and Flannery,[2] Flannery,[11] and Wadehra and Bardsley[3] to connect the low- and high-density limits and to provide an accurate theory for intermediate density. Most recently Bardsley and Wadehra[6] have performed classical-trajectory Monte Carlo calculations in an effort to avoid some of the *ad hoc* features, such as the concept of trapping radius, of the analytical calculations.

The simplest means of accounting for the effects of other ions on the recombination rate is to assume that the recombining ions interact via a screened Debye potential rather than the Coulomb potential. The Coulomb potential is damped by an exponential screening factor $\exp(-r/\lambda)$, where $\lambda = (4\pi e^2 \sum_i n_i Z_i / kT_i)^{-1/2}$ is the Debye length. In the calculation presented here we assume the temperature of any electrons to be elevated (~ 1 eV) above that of the ions and neutrals (~ 300 K). The electrons do not, therefore, contribute significantly to the screening. This potential treats ions (other than the recombining pair) as a continuous space-charge distribution. Screening effects begin to become important at ion densities of about $10^{13}$ cm$^{-3}$, when the interatomic distance becomes comparable with the Debye length. At ion densities above $10^{15}$ cm$^{-3}$ the Debye approximation, which is derived from the leading term in a cluster expansion, fails as higher-order terms become inportant.[12]

We calculate the probability of recombination by use of a Monte Carlo simulation. A detailed description of this technique has been given by Bardsley and Wadehra.[6] We will discuss it briefly here. The calculation begins with an ion pair having an initial separation $r_0$ and an initial inward relative velocity. The motion of the ions is computed as they move in classical orbits under the influence of the Debye potential and undergo collisions with the neutral gas atoms. The particles are followed until their relative energy falls below some critical value, when we assume recombination has occurred, or until their separation becomes larger than $r_0$. The initial separation must be large enough that the initial velocity distribution is Maxwellian, and small enough that there are few ions closer than $r_0$ to a given pair. We find $r_0 = 1000a_0$ to be a good choice. We found the recombination probability to be insensitive to the critical energy for energies less than about $-5kT$. We chose $E_{\text{crit}} = -12kT$. The probability of collision with a neutral is calculated by use of the Langevin ion-atom potential, which gives a constant collision frequency[13]

$$\nu^{\pm} = 2\pi N(pe^2/\mu^{\pm})^{1/2}, \tag{1}$$

where $N$ is the neutral density, $p$ is the neutral-atom polarizability, and $\mu$ is the ion-atom reduced mass.

The problem of calculating the trajectories of the ion pair can be reduced to that of a single particle moving in a central force field. The orbit around the center of force with potential $V(r)$ is described by the quadrature[14]

$$\theta = \int_{r_{c1}}^{r} \frac{dr}{r\{(2m/l^2)[E+V(r)]r^2 - 1\}^{1/2}}, \tag{2}$$

where $r_{c1}$ is the pericenter of the orbit, $E$ is the total energy, and $l$ is the angular momentum. For a Coulomb potential (2) can be integrated analytically, giving stable conic-section orbits. The Debye potential offers several complications. First, the short-range nature of the potential allows for the existence of a centrifugal barrier for large angular momenta. Thus, ion pairs with positive energy may be bound within this barrier. However, since the barrier is quite small (typically $\sim 0.01kT$), it has little effect on the recombination probability. Second, the integral (2) can no longer be performed analytically. For any potential $V(r)$ we determine $r_{c1}$ numerically and evaluate (2) numerically by repeated Gauss-Chebyshev quadrature over subintervals of the domain $(r_{c1}, r)$. This allows the singularity at the turning points of the orbit to be integrated out. For the Debye potential we have open orbits or bound orbits which precess about a constant apsidal angle.

Because the angular momentum is a constant of the motion, $\Delta\theta$ between collisions is directly proportional to $\Delta t$. Random numbers are generated to represent random collision intervals $\Delta t$ and, hence, directly provide the angular displacement and, through (2), the radial displacement in the orbit between collisions. Before a collision a random velocity is generated for the neutral, according to a Maxwellian distribution, and after the collision a new relative velocity is generated for the ion-neutral pair. A check is made to see whether the ion pair has recombined (i.e., the relative energy is less than $-12kT$). If not, the new orbit is computed and the ion pair is followed until it either leaves the sphere or again collides with a neutral atom.

At each of the pressures and densities shown in Fig. 1 we simulated ten experiments of 1000 ion pairs each. This gives a statistical uncertainty in the recombination rate of about 3%. We then calculated the recombination rate coefficient $\alpha$ from

$$\alpha = \pi r_0^2 \bar{v} w n(r_0)/n(\infty), \tag{3}$$

where $\bar{v} = (8kT/\pi\mu)^{1/2}$ is the mean velocity, $w$ is the recombination probability from the Monte Carlo simulation, $n(r_0)$ is the ion number density at $r = r_0$, and $n(\infty)$ is the average (macroscopic) ion density. Note that the apparent dependence of $\alpha$ on $r_0$ is compensated for by the variation of $w$ and $n(r_0)$. Test calculations indicate that $\alpha$ does not depend on $r_0$ provided $r_0$ satisfies the criteria mentioned above. The ion density at the edge of the sphere, $n(r_0)$, is calculated from diffusion theory.[10] The flow of ions across a spherical surface of radius $r$ is given by

$$4\pi r^2[D\,dn(r)/dr + KF(r)n(r)], \tag{4}$$

where $D$ is the diffusion coefficient, $K$ is the ionic mobility, and $F(r) = -\nabla V(r)$ is the electric field at $r$. At $r = r_0$ this flow is equal to $\alpha n(\infty)$

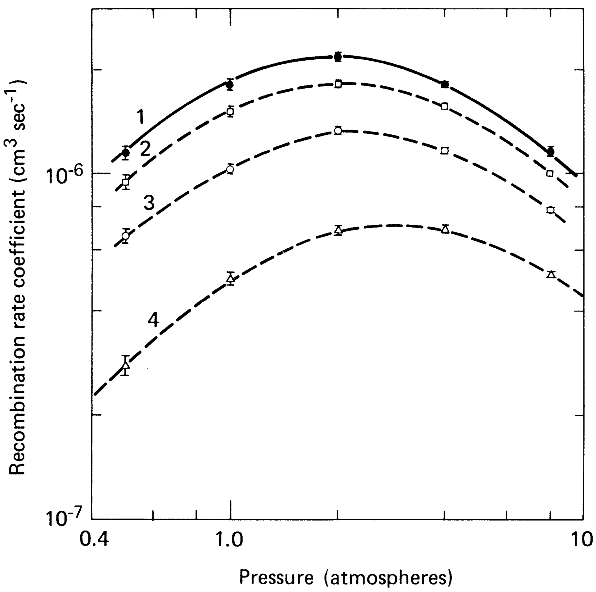


FIG. 1. Recombination rate coefficient for $Kr^+$ and $F^-$ in Ar. Solid curve, results of Ref. 6 for Coulomb potential. Points labeled with error bars, calculations for ion densities of (1) 0, (2) $10^{13}$ cm$^{-3}$, (3) $10^{14}$ cm$^{-3}$, and (4) $10^{15}$ cm$^{-3}$. The corresponding Debye lengths are $\infty$, $5050a_0$, $1600a_0$, and $505a_0$, respectively.

$=\pi r_0^2 \bar{v} w n(r_0)$. These two expressions can be set equal and the resulting differential equation solved with use of the Debye potential. Using the Einstein relation $D = kTK/e$ and letting $r \to \infty$, we can write the solution as

$$\frac{n(\infty)}{n(r_0)} = \exp\left[-\frac{e^2 \exp(-r_0/\lambda)}{r_0 kT}\right] + \frac{r_0^2 \bar{v} w e}{4kTK\lambda}\int_{r_0/\lambda}^{\infty} \exp\left(\frac{-e^2 \exp(-x)}{\lambda kTX}\right)\frac{dx}{x^2}. \quad (5)$$

This expression can now be used in (3) to calculate the recombination rate coefficient $\alpha$. Following Bardsley and Wadehra[6] we can write (3) as

$$\frac{1}{\alpha} = \frac{T_1}{\alpha_T} + \frac{e^2 T_2}{kT\lambda}\frac{1}{\alpha_L}, \quad (6)$$

where $T_1$ is the first term in Eq. (5), $T_2$ is the integral in (5), and $\alpha_T = \pi r_0^2 \bar{v} w$ and $\alpha_L = 4\pi eK$ are the Thomson and Langevin limits respectively. In the limits of high and low densities the first and second term, respectively, will dominate.

We have calculated the ionic recombination rate coefficient for $Kr^+$ and $F^-$ in Ar for five pressures and ion densities of $10^{13}$, $10^{14}$, and $10^{15}$ cm$^{-3}$ at a gas temperature of 300 K. The corresponding Debye lengths are $5050a_0$, $1600a_0$, and $505a_0$, respectively. The results are shown in Fig. 1 along with the Bardsley and Wadehra[6] Coulomb results for comparison. Plasma shielding clearly results in a significant reduction in the recombination rate. In the low-pressure (Thomson) limit the recombination process becomes purely three body and $\alpha$ will be directly proportional to the pressure. In the high-pressure (Langevin) limit the recombination is diffusion limited and the rate will be inversely proportional to the pressure. The proportionality coefficients for the low- and high-pressure limits are shown in Table I.

TABLE I. Slope of recombination rate coefficient versus pressure in the low-pressure ($P < 0.5$ atm) limit and slope of recombination rate coefficient versus inverse pressure in the high-pressure ($P > 20$ atm) limit, for various ion densities.

| Ion density (cm$^{-3}$) | Low-pressure limit (cm$^3$ s$^{-1}$ atm$^{-1}$) | High-pressure limit (cm$^3$ s$^{-1}$ atm) |
|---|---|---|
| $< 10^{13}$ [a] | $2.7\times10^{-6}$ | $1.0\times10^{-5}$ |
| $10^{13}$ | $2.1\times10^{-6}$ | $9.9\times10^{-6}$ |
| $10^{14}$ | $1.5\times10^{-6}$ | $8.1\times10^{-6}$ |
| $10^{15}$ | $6.2\times10^{-7}$ | $5.6\times10^{-6}$ |

[a] Columb potential.

As mentioned above, the Debye potential is valid up to ion densities of about $10^{15}$ cm$^{-3}$. At greater densities the higher-order correlation functions become significant. The theory of electrolytic solutions[15] suggests that the hypernetted-chain equation, which converges well for the long-range Coulomb pair potential and is valid to the fourth order in the density, will provide a better approximation to the potential at higher ionic densities.

Finally, it should be mentioned that there are no experimental data for this recombination rate with which to make comparisons. This is generally the case for ionic recombination. Nevertheless, these calculations serve to demonstrate the extent of the shielding effects and to provide data with which analytic theories of recombination can be compared.

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[1]M. R. Flannery, Int. J. Quantum Chem., Symp. 13, 501 (1979).

[2]D. R. Bates and M. R. Flannery, J. Phys. B 2, 184 (1969).

[3]J. M. Wadehra and J. N. Bardsley, Appl. Phys. Lett. 32, 76 (1978).

[4]M. R. Flannery and T. P. Yang, Appl. Phys. Lett. 33, 574 (1978).

[5]D. R. Bates and I. Mendaš, Proc. Roy Soc. London, Ser. A 359, 287 (1978).

[6]J. N. Bardsley and J. M. Wadehra, Chem. Phys. Lett. 72, 477 (1980).

[7]R. K. Janev and Z. M. Radulovic, J. Chem. Phys. 67, 2856 (1977).

[8]J. J. Thomson, Philos. Mag. 47, 337 (1924).

[9]P. Langevin, Ann. Chem. Phys. 48, 433 (1903).

[10]G. L. Natanson, Zh. Tekh. Fiz. 29, 1373 (1959) [Sov. Phys. Tech. Phys. 4, 1263 (1959)].

[11]M. R. Flannery, Chem. Phys. Lett. 56, 143 (1978).

[12]J. C. Rasaiah and H. L. Friedman, J. Chem. Phys. 48, 2742 (1968).

[13]E. W. McDaniel, V. Cermak, A. Dalgarno, E. E. Ferguson, and L. Friedman, *Ion-Molecule Reactions* (Wiley-Interscience, New York, 1970).

[14]H. Goldstein, *Classical Mechanics* (Addison-Wesley, Reading, Mass., 1950).

[15]J. A. Barker and D. Henderson, Rev. Mod. Phys. 48, 587 (1976).