Moment Theory of Ion-Neutral Reactions in Traps and Similar Devices

Larry A. Viehland,*,† Daniel M. Danailov,† and Douglas E. Goeringer‡

Science Division, Chatham College, Pittsburgh, Pennsylvania 15232-2813, and
Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6131

Received: September 18, 2006; In Final Form: February 5, 2007

Recent moment theories of ion motion in traps and similar devices are extended to mixtures of neutral gases in which one or more components can undergo infrequent reaction with the ion of interest. Expressions are developed for the position and time dependence of the ion-neutral reaction rate coefficient in such circumstances. These expressions are incorporated into the sets of coupled differential equations that govern the average ion velocity and kinetic and internal energies. This provides a consistent description of the ion transport and reaction coefficients.

1. Introduction

Gas-phase ion−molecule reactions are of considerable interest, from both applied and fundamental standpoints, because they are important processes in areas such as mass spectrometry, atmospheric chemistry, and combustion. Consequently, numerous reactions of this type have been investigated and their reaction rate data compiled.[1−3] For atomic ion reactions with atomic neutrals, the true thermal reaction rate coefficient, $k_R^{(0)}(T)$, as a function of temperature, T, is obtained by averaging the integral reaction cross-section, Q_R^*, over a Maxwellian distribution of relative reactant energies, E_{rel}. When Q_R^* is normalized so that it is equal to πd^2 for the reaction of rigid spheres of diameter d, the textbook expression[4] is

$$k_R^{(0)}(T) = \frac{1}{k_BT}\left(\frac{2}{\pi\mu_R k_BT}\right)^{1/2} \int_0^\infty E_{rel} \exp\left(-\frac{E_{rel}}{k_BT}\right) Q^*(E_{rel})\, dE_{rel} \tag{1}$$

where μ_R is the reduced mass of the ion and neutral reactants, k_B is Boltzmann's constant, and the superscript 0 is used as a reminder of the assumption of a nearly Maxwellian distribution. Because the relative kinetic energy is equal to $(^3/_2)k_BT$ for thermal collisions, eq 1 may be written in the alternative form,

$$k_R^{(0)}(T) = \left(\frac{8k_BT}{\pi\mu_R}\right)^{1/2} \int_0^\infty \exp(-\gamma^2) Q_R^*(\gamma^2 k_BT)\gamma^3\, d\gamma \tag{2}$$

Although it is often of interest to acquire high-temperature, thermal rate coefficients for ion−molecule reactions, raising the operating temperature of typical apparatus above ~900 K by conventional heating methods is problematic. Alternatively, it is possible to increase the temperature above that limit (and have more flexibility below it) by electric field acceleration of the ions. Suppose that we are concerned with atomic ions drifting through a dilute atomic gas under the influence of a uniform, electrostatic field of arbitrary strength. For this situation, the mean kinetic energy, $\langle E_{ion}\rangle$, for ions of mass, m, moving at velocity, v_d, through an inert buffer gas having mass, M, was determined from basic principles by Wannier[6] for the Maxwell model, where the particles interact as a point-charge ion and a neutral with an induced dipole. Wannier's expression is

$$\langle E_{ion}\rangle = \frac{3}{2}k_BT + \frac{1}{2}mv_d^2 + \frac{1}{2}Mv_d^2 \tag{3}$$

where the first term is the thermal energy, the second is the energy that the ions have gained from the electrostatic field and are exhibiting as motion along that field, and the third is the field energy that has been transformed into random motion due to collisions with the neutral particles.

Transforming eq 3 into the center-of-mass for an ion-neutral collision then yields the average collision energy,

$$\langle E_{CM}\rangle = \frac{3}{2}k_BT + \frac{1}{2}Mv_d^2 \tag{4}$$

If reactant molecules (with mass M_R) are added to the buffer gas at a number density low enough that ion−reactant encounters are relatively rare events, then $\langle E_{rel}\rangle$ for the ion−molecule reaction is given by the equation[7]

$$\langle E_{rel}\rangle = \frac{3}{2}k_BT + \left(\frac{m+M_R}{m+M}\right)\left(\frac{1}{2}M_Rv_d^2\right) = \frac{3}{2}k_BT_R^{(eff)} \tag{5}$$

Here $T_R^{(eff)}$ is the effective temperature characterizing the relative reactant energy, $\langle E_{rel}\rangle$, but it has no direct relationship to the distribution functions of the ions or neutrals.

Although rigorously correct only for the Maxwell model of constant collision frequencies, eqs 3−5 have been shown[8] to be correct within 10% for virtually all atomic ion−atom systems. For an apparatus in which the electric field, E, and the buffer gas number density, N, are constant, it is straightforward to determine v_d, and thus $T_R^{(eff)}$. The above suggests, therefore, that the reaction rate coefficient measured under such conditions, $k_R(T,E/N)$, should be nearly identical with the thermal rate coefficient determined at $T_R^{(eff)}$, viz.,

$$k_R^{(0)}(T_R^{(eff)}) = \left(\frac{8k_BT_R^{(eff)}}{\pi\mu_R}\right)^{1/2} \int_0^\infty \exp(-\gamma^2) Q_R^*(\gamma^2 k_BT_R^{(eff)})\gamma^3\, d\gamma \tag{6}$$

Consequently, several techniques, such as drift tubes,[8,9] drift tube mass spectrometers[10] (DTMS), selected ion drift

---

* To whom correspondence should be addressed. E-mail: viehland@chatham.edu.
† Chatham College.
‡ Oak Ridge National Laboratory.

10.1021/jp066096m CCC: $37.00

apparatus (SIDA),[11,12] flow tubes,[13,14] etc.,[15] have been used to investigate ion−molecule reactions as a function of electric field strength (or more correctly, the ratio E/N).

Although the velocity distribution of reactant (and buffer gas) neutrals is Maxwellian for the thermal techniques, a difficulty arises if $k_R(T,E/N)$ is construed as a thermal rate coefficient: the actual velocity distribution of the reactant ions is not known, but it is certainly not Maxwellian. That is, $\langle E_{\text{ion}}\rangle$ and then $T_R^{(\text{eff})}$ determined from a measured v_d value are approximations and, even if they are accurate, any number of distribution functions besides a Maxwellian can have the same v_d and $\langle E_{\text{ion}}\rangle$. Additional complications arise if polyatomic ions are involved because collisions with the buffer gas atoms increase the internal energy of these molecular ions. Thus, the ion internal temperature, T_{int}, and the corresponding internal state distribution function, must then be considered. For situations involving molecular neutrals as well, their internal state distribution also has to be taken into account. General moment theories, based on transformation of the Boltzmann equation, have been developed for the situations described above, initially for the reaction of atomic ions and atomic gases in electrostatic fields,[16] and later for drift tube reactions of polyatomic species.[7] These theories indicate that ion−molecule reaction rate coefficients, $k_R(T,E/N)$, measured as a function of gas temperature and electric field strength are indeed equivalent to thermal rate coefficients, $k_R^{(0)}(T_R^{(\text{eff})})$. The difficulty is therefore conceptual and not real.

The situation is even more complicated for the reaction of trace amounts of ions in dilute neutral gases when the charged particles are under the influence of external fields that vary with time and with position in the apparatus.[17,18] In five recent papers,[19−23] we developed general theories for ion motion under such conditions and applied them to field-asymmetric ion mobility spectrometers and three-dimensional quadrupole ion traps. The purposes of this paper are to derive expressions for the ion velocity distribution function and the rate coefficients for ion-neutral reactions and to obtain the moment equations that describe the average ion velocity and energy in a gas mixture. To this end, we consider in Section 2 the two-temperature (2T) and multitemperature (MT) moment theories[19] for atomic ions and neutrals. In Section 3, we consider the spherical-basis (SB) and Cartesian-basis (CB) moment theories[22] for molecular ions and neutrals. Applications of our results are given in Section 4 and a discussion in Section 5.

As noted earlier, we are concerned with experiments in which reactive ion-neutral encounters are infrequent, either because the neutral gas consists of a small amount of a reactive gas immersed in a large amount of a nonreactive, buffer gas, or because most of the potentially reactive collisions are actually unreactive for mechanistic or energetic reasons. We let x_j and N_j be the mole fraction and number density of gas j, so that the total number density of the gas is

$$N = \sum_j x_j N_j \tag{7}$$

Because only trace amounts of ions are used, ion−ion collisions can be neglected, and we need consider here only one particular ion species. For simplicity, we will also restrict our attention to situations where the only external fields are electrical.

2. Atomic Systems

In this section, we consider trace amounts of an atomic ion moving through a dilute neutral gas that is predominantly nonreactive and is composed of a mixture of atomic gases. On a microscopic level, collisions between the ions of interest and neutral atoms of species j are described by the integral cross-section for reaction, Q_j^*, and the differential cross-section for elastic scattering, σ_j. Both cross-sections are functions of the relative kinetic energy,

$$\epsilon_j = \frac{\mu_j}{2}|\mathbf{v} - \mathbf{V}_j|^2 \tag{8}$$

in the center-of-mass frame of the colliding particles, and σ_j is also a function of the scattering solid angle, $\Omega_j = \{\theta_j, \phi_j\}$. Here

$$\mu_j = \frac{mM_j}{m + M_j} \tag{9}$$

is the reduced mass for the ion of mass m with velocity v in the laboratory frame of reference and the neutral of species j with mass M_j and velocity V_j.

Macroscopic properties of the ion motion through the gas mixture can always be expressed in terms of moments with respect to the ion distribution function, f, that is a function of the time, t, the ion position, $\mathbf{r}$, and $\mathbf{v}$. For the circumstances described above, the distribution function is governed by the following version[16] of the Boltzmann equation:

$$\left[\frac{\partial}{\partial t} + \mathbf{v}\cdot\nabla + \frac{q}{m}\mathbf{E}(\mathbf{r},t)\cdot\nabla_v + \sum_j \int F_j(\mathbf{V}_j)Q_j^*(\epsilon_j)\left|\mathbf{v} - \mathbf{V}_j\right| \mathrm{d}\mathbf{V}_j\right] \times f(\mathbf{r},\mathbf{v},t) = \sum_j \mathscr{J}_j f(\mathbf{r},\mathbf{v},t) \tag{10}$$

Here q is the ion charge, $\mathbf{E}(\mathbf{r},t)$ is the external electric field whose dependences upon position and time are assumed to be known, the center dot (•) indicates the scalar product of the two vectors surrounding it, and the quantities $(\partial/\partial t)$, ∇ and ∇_v are gradient operators in time, position, and velocity space, respectively. The nonreactive Boltzmann operator on the right-hand side of eq 10 is defined by the expression

$$\mathscr{J}_j f(\mathbf{r},\mathbf{v},t) = \int [f(\mathbf{r},\mathbf{v}',t)F_j(\mathbf{V}_j') - f(\mathbf{r},\mathbf{v},t)F_j(\mathbf{V}_j)] \times |\mathbf{v} - \mathbf{V}_j|\sigma_j(\epsilon_j,\theta_j)\sin(\theta_j)\,\mathrm{d}\theta_j\,\mathrm{d}\phi_j\,\mathrm{d}\mathbf{V}_j \tag{11}$$

where the primes represent postcollision velocities that are connected to their precollision (unprimed) counterparts by conservation of energy and linear momentum and by the details of the ion-neutral interaction potential that governs $\sigma_j(\epsilon_j,\theta_j)$. Finally, the distribution functions for the neutrals at gas temperature T have the equilibrium, Maxwellian form,

$$F_j(\mathrm{V}) = N_j\left(\frac{M_j}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{M_j V_j^2}{2k_B T}\right) \tag{12}$$

Rather than solving eq 10 and then throwing away much of the hard-won information by integrating to calculate the desired moments, the essential feature of our previous work[19] is to transform the Boltzmann equation into moment equations, i.e., a set of partial differential equations that governs directly the moments of interest. There are only two differences between eq 10 and the Boltzmann equation used previously.[19] The first is that the right-hand side involves a sum of collision terms involving each of the neutral gases. The other, more significant difference is that there is a reactive term on the left-hand side. Because reactions are assumed to be infrequent, this term can be dropped in all situations where the nonreactive term does not vanish. This means that the reactive term is not dropped when the equation of continuity is obtained by integrating the Boltzmann equation over all velocities. We thus obtain the rate equation of continuity,

$$\frac{\partial}{\partial t}n(\mathbf{r},t) + \nabla\cdot n(\mathbf{r},t)\bar{\mathbf{v}}(\mathbf{r},t) = -n(\mathbf{r},t)\,N\,k(\mathbf{r},t) \tag{13}$$

where the ion number density is

$$n(\mathbf{r},t) = \int f(\mathbf{r},\mathbf{v},t)\,\mathrm{dv} \tag{14}$$

the average ion velocity is

$$\bar{\mathbf{v}}(\mathbf{r},t) = \frac{\int f(\mathbf{r},\mathbf{v},t)\mathbf{v}\,\mathrm{d}\mathbf{v}}{n(\mathbf{r},t)} \tag{15}$$

and the two-body reaction rate coefficient is

$$k(\mathbf{r},t) = \sum_j x_j \int\int \left[\frac{f(\mathbf{r},\mathbf{v},t)}{n(\mathbf{r},t)}\right]\left[\frac{F_j(\mathbf{V}_j)}{N_j}\right] Q_j^*(\epsilon_j)|\mathbf{v}-\mathbf{V}_j|\,\mathrm{d}\mathbf{V}_j\,\mathrm{d}\mathbf{v} \tag{16}$$

The dependence of $k(\mathbf{r},t)$ upon position and time, like that of the ion velocity distribution function, arises because the ion energy depends upon the strengths of the external fields that act upon the ions, and these fields may be position- or time-dependent. In eq 16, we have left implicit the dependence upon the gas temperature, T, and we have assumed the reaction cross-section, Q_j^*, is provided from some experiment or theory outside of the present work, as a function of ϵ_j.

To change eq 10 into equations governing moments of the ion velocity distribution function, we start with eq I-17, i.e., with eq 17 of the first paper:[19]

$$f(\mathbf{r},\mathbf{v},t) = n(\mathbf{r},t)f_0(\mathbf{r},\mathbf{v},t)\sum_{l,m,n} c_{l,m,n}(\mathbf{r},t)\Psi_{l,m,n}(\mathbf{r},\mathbf{v},t) \tag{17}$$

This equation indicates that the distribution function has been expanded in terms of $n(\mathbf{r},t)$, a zero-order approximation function, $f_0(\mathbf{r},\mathbf{v},t)$, and a set of basis functions $\Psi_{l,m,n}(\mathbf{r},\mathbf{v},t)$. A series of systematic approximations for obtaining the expansion coefficients, $c_{l,m,n}(\mathbf{r},t)$, with increasing accuracy has been described previously.[19] The convergence of this series depends upon the particular choices made, and these in turn depend upon the symmetry and other properties of the experiment of interest.

2.1. Two-Temperature Theory. The 2T theory uses the choices

$$f_0^{(2T)}(\mathbf{r},\mathbf{v},t) = \left(\frac{m}{2\pi k_\mathrm{B}T_\mathrm{ion}(\mathbf{r},t)}\right)^{3/2}\exp(-W^2) \tag{18}$$

and

$$\Psi_{l,m,n}^{(2T)}(\mathbf{r},\mathbf{v},t) = W^l S_{l+1/2}^{(n)}(W^2)Y_l^m(\hat{\mathbf{W}}) \tag{19}$$

where

$$\mathbf{W}(\mathbf{r},\mathbf{v},t) = \left(\frac{m}{2k_\mathrm{B}T_\mathrm{ion}(\mathbf{r},t)}\right)^{1/2}\mathbf{v} \tag{20}$$

Here $S_{l+1/2}^{(n)}(W^2)$ is a Sonine (associated Laguerre) polynomial of the square of the magnitude of $\mathbf{W}$, $Y_l^m(\hat{\mathbf{W}})$ is a spherical harmonic of the angles of $\mathbf{W}$, and $T_\mathrm{ion}(\mathbf{r},t)$ is the ion temperature. Because the ions are present only in trace amounts, $T_\mathrm{ion}(\mathbf{r},t)$ can be substantially larger than T; it is determined by constraining the solution of the moment equations that give the $c_{l,m,r}(\mathbf{r},t)$ so that

$$\frac{3}{2}k_\mathrm{B}T_\mathrm{ion}(\mathbf{r},t) = \frac{\int f(\mathbf{r},\mathbf{v},t)\left[\frac{1}{2}mv^2\right]\mathrm{d}\mathbf{v}}{n(\mathbf{r},t)} \tag{21}$$

Note how the position and time dependence of $f_0^{(2T)}(\mathbf{r},\mathbf{v},t)$ and $\Psi_{l,m,r}^{(2T)}(\mathbf{r},\mathbf{v},t)$ arise indirectly through their dependences upon $T_\mathrm{ion}(\mathbf{r},t)$; in paper I,[19] these dependences were left implicit.

Equation I-28[19] indicates that we must have

$$c_{0,0,0}^{(2T)}(\mathbf{r},t) = (4\pi)^{1/2} \tag{22}$$

in order for the zero-order distribution function to be properly normalized. For the moments of the ion velocity (i.e., eq 15) to be correct, we must have

$$c_{1,0,0}^{(2T)}(\mathbf{r},t) = 2\left(\frac{4\pi}{3}\right)^{1/2}\overline{W_z}(\mathbf{r},t) \tag{23}$$

$$c_{1,1,0}^{(2T)}(\mathbf{r},t) = -\left(\frac{2\pi}{3}\right)^{1/2}(\overline{W_y}(\mathbf{r},t) + i\,\overline{W_x}(\mathbf{r},t)) \tag{24}$$

and

$$c_{1,-1,0}^{(2T)}(\mathbf{r},t) = \left(\frac{2\pi}{3}\right)^{1/2}(\overline{W_y}(\mathbf{r},t) - i\,\overline{W_x}(\mathbf{r},t)) \tag{25}$$

where the $\overline{W_u}(\mathbf{r},t)$ are velocity averages of the Cartesian components of eq 20 for $u = x,y,z$. Finally, we find that in order to satisfy eq 21, it is necessary that

$$c_{0,0,1}^{(2T)}(\mathbf{r},t) = 0 \tag{26}$$

In first approximation, all of the other expansion coefficients in eq 17 are equal to zero. When eqs 22–26 are combined with the explicit expressions for the corresponding basis functions, then the first approximation to eq 17 becomes

$$f(\mathbf{r},\mathbf{v},t) = n(\mathbf{r},t)f_0^{(2T)}(\mathbf{r},\mathbf{v},t)[1 + 2\sum_u \overline{W_u}(\mathbf{r},t)W_u(\mathbf{r},\mathbf{v},t)] \tag{27}$$

This equation is deceptively simple because the dependences upon $\mathbf{r}$ and t occur through $T_\mathrm{ion}(\mathbf{r},t)$ while both $T_\mathrm{ion}(\mathbf{r},t)$ and $\overline{W_u}(\mathbf{r},t)$ must be obtained by solving differential equations, as shown below.

By making use of eqs 12, 17, 18, and 27, eq 16 can be written in first approximation as

$$k^{(2T)}(\mathbf{r},t) = \sum_j\left(\frac{M_j}{2\pi k_\mathrm{B}T}\right)^{3/2}\left(\frac{m}{2\pi k_\mathrm{B}T_\mathrm{ion}(\mathbf{r},t)}\right)^{3/2}\times \int\int\exp\left(-\frac{M_jV_j^2}{2k_\mathrm{B}T} - \frac{mv^2}{2k_\mathrm{B}T_\mathrm{ion}(\mathbf{r},t)}\right)\times \left[1 + 2\left(\frac{m}{2k_\mathrm{B}T_\mathrm{ion}(\mathbf{r},t)}\right)^{1/2}\sum_u\overline{W_u}(\mathbf{r},t)v_u\right]|\mathbf{v}-\mathbf{V}_j|Q_j^*(\epsilon_j)\,\mathrm{d}\mathbf{V}_j\,\mathrm{d}\mathbf{v} \tag{28}$$

If the ion and neutral temperatures were the same, we could simplify eq 28 by introducing the relative and center-of-mass velocities. To get a simple term in the exponent, however, we must here introduce the new vectors

$$\chi = \left[\frac{mT + M_j T_{\mathrm{ion}}(\mathbf{r},t)}{2k_{\mathrm{B}} T T_{\mathrm{ion}}(\mathbf{r},t)}\right]^{1/2} \frac{mT\mathbf{v} + M_j T_{\mathrm{ion}}(\mathbf{r},t)\mathbf{V}_j}{mT + M_j T_{\mathrm{ion}}(\mathbf{r},t)} \tag{29}$$

and

$$\gamma = \left[\frac{mM_j}{2k_{\mathrm{B}}\{mT + M_j T_{\mathrm{ion}}(\mathbf{r},t)\}}\right]^{1/2} (\mathbf{v} - \mathbf{V}_j) \tag{30}$$

In terms of these vectors, whose time- and position-dependences have been left implicit, eq 28 can be written as

$$k^{(2\mathrm{T})}(\mathbf{r},t) = \frac{1}{\pi^3} \sum_j x_j \left[\frac{2k_{\mathrm{B}} T_j^{(\mathrm{eff})}(\mathbf{r},t)}{\mu_j}\right]^{1/2} \int\int \exp(-\gamma^2 - \chi^2) \times \left[1 + 2\sum_u \overline{W_u}(\mathbf{r},t)\left\{\left(\frac{mT}{mT + M_j T_{\mathrm{ion}}(\mathbf{r},t)}\right)^{1/2} \chi_u + \left(\frac{M_j T_{\mathrm{ion}}(\mathbf{r},t)}{mT + M_j T_{\mathrm{ion}}(\mathbf{r},t)}\right)^{1/2} \gamma_u\right\}\right] \gamma Q_j^*(\gamma^2 k_{\mathrm{B}} T_j^{(\mathrm{eff})}(\mathbf{r},t))\, \mathrm{d}\chi\, \mathrm{d}\gamma \tag{31}$$

where the effective temperature is

$$T_j^{(\mathrm{eff})}(\mathbf{r},t) = \frac{mT + M_j T_{\mathrm{ion}}(\mathbf{r},t)}{m + M_j} \tag{32}$$

The integration over χ is easy, giving

$$k^{(2\mathrm{T})}(\mathbf{r},t) = \frac{1}{\pi^{3/2}} \sum_j x_j \left[\frac{2k_{\mathrm{B}} T_j^{(\mathrm{eff})}(\mathbf{r},t)}{\mu_j}\right]^{1/2} \int \exp(-\gamma^2) \times \left[1 + 2\left(\frac{M_j T_{\mathrm{ion}}(\mathbf{r},t)}{mT + M_j T_{\mathrm{ion}}(\mathbf{r},t)}\right)^{1/2} \sum_u \overline{W_u}(\mathbf{r},t)\gamma_u\right] \times \gamma Q_j^*(\gamma^2 k_{\mathrm{B}} T_j^{(\mathrm{eff})}(\mathbf{r},t))\, \mathrm{d}\gamma \tag{33}$$

Finally, we can integrate over the angles of γ to get

$$k^{(2\mathrm{T})}(\mathbf{r},t) = \sum_j x_j \left[\frac{8k_{\mathrm{B}} T_j^{(\mathrm{eff})}(\mathbf{r},t)}{\pi\mu_j}\right]^{1/2} \times \int_0^\infty \exp(-\gamma^2) Q_j^*(\gamma^2 k_{\mathrm{B}} T_j^{(\mathrm{eff})}(\mathbf{r},t))\gamma^3\, \mathrm{d}\gamma \tag{34}$$

This has the same form as eq 6 and is the same expression as would have been obtained by using the zero-order distribution function rather than the first approximation to the ion distribution function; the additional terms in first approximation disappear when computing the reaction rate coefficient.

We now have explicit expressions for the ion velocity distribution function and the reaction rate coefficient in first approximation of the 2T theory. However, these expressions involve the average ion velocity, ion temperature, and effective temperature. To complete the description of the motion of atomic ions in quadrupole ion traps filled with a mixture of atomic gases, we must analyze eq 10 in the same way we analyzed previously[19] the Boltzmann equation for a single-component gas. Fortunately, this is a straightforward but tedious extension of the same steps, so it suffices here to simply cite the final results. The differential equation governing the average velocity of the ion swarm in first approximation is

$$\frac{\partial}{\partial t}\bar{\mathbf{v}} - \frac{q}{m}\mathbf{E} + \xi^{(2\mathrm{T})}(T_{\mathrm{ion}})\bar{\mathbf{v}} = 0 \tag{35}$$

where the time- and position-dependence of T_{ion} has been left implicit. The total momentum transfer collision frequency is a linear combination of those for each gas, i.e.,

$$\xi^{(2\mathrm{T})}(T_{\mathrm{ion}}) = \sum_j x_j \xi_j^{(2\mathrm{T})}(T_{\mathrm{ion}}) \tag{36}$$

where

$$\xi_j^{(2\mathrm{T})}(T_{\mathrm{ion}}) = \frac{8N}{3} \frac{M_j}{m + M_j} \left(\frac{2k_{\mathrm{B}} T_j^{(\mathrm{eff})}(\mathbf{r},t)}{\pi\mu_j}\right)^{1/2} \bar{\Omega}^{(1,1)}(T_j^{(\mathrm{eff})}(\mathbf{r},t)) \tag{37}$$

and $\bar{\Omega}^{(1,1)}$ is the momentum-transfer collision integral.[8] Because there is a different effective temperature, $T_j^{(\mathrm{eff})}(\mathbf{r},t)$, for each gas j, the first approximation moment equation for the kinetic energy of the ion swarm must be left as a differential equation for T_{ion} rather than, as in paper I,[19] converted to a differential equation for the effective temperature. This moment equation is

$$\frac{\partial}{\partial t}T_{\mathrm{ion}} - \frac{2q}{3k_{\mathrm{B}}}\mathbf{E}\cdot\bar{\mathbf{v}} + \left[\sum_j x_j \frac{2m\xi_j^{(2\mathrm{T})}(T_{\mathrm{ion}})}{m + M_j}\right][T_{\mathrm{ion}} - T] = 0 \tag{38}$$

and after it is solved, the various $T_j^{(\mathrm{eff})}(\mathbf{r},t)$ can be obtained by using eq 32. This completes the first approximation of the 2T theory, which will be discussed further in Section 4.

2.2. Multitemperature Theory. The MT theory for atomic ions and neutrals uses the choices

$$f_0^{(\mathrm{MT})}(\mathbf{r},\mathbf{v},t) = \prod_{u=x,y,z} \left(\frac{m}{2\pi k_{\mathrm{B}} T_u(\mathbf{r},t)}\right)^{1/2} \exp(-W_u^2) \tag{39}$$

and

$$\Psi_{l,m,n}^{(\mathrm{MT})}(\mathbf{r},\mathbf{v},t) = H_l(W_x)H_m(W_y)H_n(W_z) \tag{40}$$

where

$$W_u(\mathbf{r},\mathbf{v},t) = \left(\frac{m}{2k_{\mathrm{B}} T_u(\mathbf{r},t)}\right)^{1/2} \mathrm{v}_u(\mathbf{r},t) \tag{41}$$

Here $H_l(W_x)$ is a Hermite polynomial of the x component of $\mathbf{W}$. The ion temperatures are determined by constraining the solution of the moment equations for the $c_{l,m,n}^{(\mathrm{MT})}(\mathbf{r},t)$ so that

$$\frac{1}{2}k_{\mathrm{B}} T_u(\mathbf{r},t) = \int f(\mathbf{r},\mathbf{v},t)\left[\frac{1}{2}m\mathrm{v}_u^2\right] \mathrm{d}\mathbf{v} \tag{42}$$

Equation I-70[19] indicates that we must have

$$c_{0,0,0}^{(\mathrm{MT})}(\mathbf{r},t) = 1 \tag{43}$$

in order for the zero-order distribution function to be properly normalized. For eq 15 to be correct, we must have

$$c_{1,0,0}^{(\mathrm{MT})}(\mathbf{r},t) = \overline{W_x}(\mathbf{r},t) \tag{44}$$

$$c_{0,1,0}^{(\mathrm{MT})}(\mathbf{r},t) = \overline{W_y}(\mathbf{r},t) \tag{45}$$

and

$$c_{0,0,1}^{(\mathrm{MT})}(\mathbf{r},t) = \overline{W_z}(\mathbf{r},t) \qquad (46)$$

Finally, we find that in order to satisfy eq 42, it is necessary that

$$c_{2,0,0}^{(\mathrm{MT})}(\mathbf{r},t) = c_{0,2,0}^{(\mathrm{MT})}(\mathbf{r},t) = c_{0,0,2}^{(\mathrm{MT})}(\mathbf{r},t) = 0 \qquad (47)$$

All other expansion coefficients are identically equal to zero in first approximation.

When these explicit results for the expansion coefficients are combined with the explicit expressions for the corresponding basis functions, then the first approximation to eq 17 becomes similar to eq 27:

$$f(\mathbf{r},\mathbf{v},t) = n(\mathbf{r},t) f_0^{(\mathrm{MT})}(\mathbf{r},\mathbf{v},t)[1 + 2 \sum_u \overline{W_u}(\mathbf{r},t) W_u(\mathbf{r},\mathbf{v},t)] \qquad (48)$$

This means that we can follow the same pattern for determining the rate coefficient as used previously. The final result is that

$$k(\mathbf{r},t) = \frac{1}{\pi} \sum_j x_j \left[\frac{2k_{\mathrm{B}}T}{\pi\mu_j}\right]^{1/2} \int\int\int \exp(-\gamma_x^2 - \gamma_y^2 - \gamma_z^2) \times Q_j^*(\epsilon_j^*(\mathbf{r},t)) \left(\frac{\epsilon_j^*(\mathbf{r},t)}{k_{\mathrm{B}}T}\right)^{1/2} \mathrm{d}\gamma_x \, \mathrm{d}\gamma_y \, \mathrm{d}\gamma_z \qquad (49)$$

where

$$\epsilon_j^*(\mathbf{r},t) = \gamma_x^2 k_{\mathrm{B}} T_{x,j}^{(\mathrm{eff})}(\mathbf{r},t) + \gamma_y^2 k_{\mathrm{B}} T_{y,j}^{(\mathrm{eff})}(\mathbf{r},t) + \gamma_z^2 k_{\mathrm{B}} T_{z,j}^{(\mathrm{eff})}(\mathbf{r},t) \qquad (50)$$

and

$$T_{u,j}^{(\mathrm{eff})}(\mathbf{r},t) = \frac{mT + M_j T_u(\mathbf{r},t)}{m + M_j} \qquad (51)$$

Equation 49 reduces to the two-temperature expression, eq 34, when the three ion temperatures, $T_u(\mathbf{r},t)$, of the MT theory are set equal to the single ion temperature, $T_{\mathrm{ion}}(\mathbf{r},t)$, of the 2T theory.

When the previous MT theory[19] is extended to gas mixtures, the differential equation governing any component of the average velocity of the ion swarm in first approximation is

$$\frac{\partial}{\partial t}\overline{v_u} - \frac{q}{m}E_u + \xi_u^{(\mathrm{MT})}(T_x,T_y,T_z)\overline{v_u} = 0 \qquad (52)$$

where

$$\xi_u^{(\mathrm{MT})}(T_x,T_y,T_z) = \sum_j x_j \xi_{u,j}^{(\mathrm{MT})}(T_x,T_y,T_z) \qquad (53)$$

and

$$\xi_{u,j}^{(\mathrm{MT})}(T_x,T_y,T_z) = \frac{2N}{\pi^{3/2}} \frac{M_j}{m + M_j} \int\int\int \exp(-\gamma_x^2 - \gamma_y^2 - \gamma_z^2)\gamma_u^2 \, g_j Q^{(1)}(\epsilon_j^*(\mathbf{r},t)) \, \mathrm{d}\gamma_x \, \mathrm{d}\gamma_y \, \mathrm{d}\gamma_z \qquad (54)$$

Because $Q^{(1)}$ is the same momentum-transfer cross-section[8] that is needed to compute $\bar{\Omega}^{(1,1)}$, eq 54 reduces to eq 37 when the three $T_u(\mathbf{r},t)$ are each set equal to $T_{\mathrm{ion}}(\mathbf{r},t)$.

The differential equation governing the average ion energies in first approximation is a generalization of eq I-88.[19] Dropping the magnetic field terms, the first approximation version of this equation is

$$\frac{\partial}{\partial t}T_u - \frac{2q}{k_{\mathrm{B}}}E_u\overline{v_u} + \left[\sum_j x_j \xi_j^{(\mathrm{MT})}(T_x,T_y,T_z)\frac{2m}{m + M_j}\right][T_u - T] + 2\sum_j x_j \xi_{u,j}^{(\mathrm{MT})}(T_x,T_y,T_z)\Phi_{u,j}^{(\mathrm{MT})}(T_x,T_y,T_z)T_{u,j}^{(\mathrm{eff})} = 0 \qquad (55)$$

The dimensionless quantity $\Phi_{u,j}^{(\mathrm{MT})}(T_x,T_y,T_z)$ allows energy partitioning[24] to occur, as described in Appendix A of paper V.[23] This completes the first approximation of the MT theory, as discussed further in Section 4.

3. Molecular Theories

On a microscopic level, collisions between the molecular ions of interest and neutral molecules of species j are described by the integral cross-section for reaction, Q_j^*, and the differential cross-section for elastic scattering, σ_j. Both cross-sections are functions of the relative kinetic energy, ϵ_j, in the center-of-mass frame of the colliding particles, and the precollision internal states, α and β, of the ion and neutral, respectively. In addition, σ_j is also a function of the scattering solid angle, Ω_j, and the postcollision states, α′ and β', of the ion and neutral.

For molecular ions, the macroscopic properties of the ion motion through a gas mixture can always be expressed as moments of the ion distribution function that depends upon the time, the ion position, the ion velocity in the laboratory frame of reference, and the ion internal state. The distribution function can, in principle, be obtained by solving the Wang−Chang−Uhlenbeck−de Boer (WCUB) equation,[7,25] which becomes

$$\left[\frac{\partial}{\partial t} + v\cdot\nabla + \frac{q}{m}\mathbf{E}(\mathbf{r},t)\cdot\nabla_v + \sum_j \sum_\beta \int F_j^{(\mathrm{B})}(\mathbf{V}_j)Q_j^*(\alpha\beta;\epsilon_j) \times \left|\mathbf{v} - \mathbf{V}_j\right| \mathrm{d}\mathbf{V}_j\right] \times f^{(\alpha)}(\mathbf{r},\mathbf{v},t) = \sum_j \mathrm{J}_j f^{(\alpha)}(\mathbf{r},\mathbf{v},t) \qquad (56)$$

when magnetic field terms are ignored. Here we assume that the cross-section, $Q^*(\alpha,\beta;\, \epsilon_{\mathrm{R}})$, for reaction between an ion in state α and a neutral molecule in state β is provided from some experiment or theory outside of the present work as a function of the reactive collision energy given by eq 8.

The nonreactive WCUB operator on the right-hand side of eq 56 is defined by the expression

$$\mathrm{J}_j f^{(\alpha)}(\mathbf{r},\mathbf{v},t) = \sum_{\alpha',\beta,\beta'} \int [f^{(\alpha')}(\mathbf{r},\mathbf{v}',t)F_j^{(\beta')}(\mathbf{V}_j') - f^{(\alpha)}(\mathbf{r},\mathbf{v},t) \times F_j^{(\beta)}(\mathbf{V}_j)]\, |\mathbf{v} - \mathbf{V}_j|\sigma_j(\alpha\beta;\alpha'\beta';\epsilon_j,\theta_j,\phi_j) \sin(\theta_j)\, \mathrm{d}\theta_j \, \mathrm{d}\phi_j \, \mathrm{d}\mathbf{V}_j \qquad (57)$$

where the primes represent postcollision velocities and internal states that are connected to their precollision (unprimed) counterparts by conservation of energy, linear momentum, and angular momentum, and by the details of the ion-neutral interaction potential that governs $\sigma_j(\alpha\beta;\, \alpha'\beta';\, \epsilon_j,\theta_j,\phi_j)$. Finally, the distribution functions for the neutrals at gas temperature T have the Maxwell−Boltzmann form,

$$F_j^{(\beta)}(\mathbf{V}) = \frac{N_j}{Z_j}\left(\frac{M_j}{2\pi k_{\mathrm{B}}T}\right)^{3/2} \exp\left(-\frac{M_j V_j^2}{2k_{\mathrm{B}}T} - \frac{\epsilon_j^{(\beta)}}{k_{\mathrm{B}}T}\right) \qquad (58)$$

where

$$Z_j = \sum_\beta \exp\left(-\frac{\epsilon_j^{(\beta)}}{k_{\mathrm{B}}T}\right) \qquad (59)$$

is the partition function for the neutrals of species j, and $\epsilon_j^{(\beta)}$ is the internal energy when the neutrals are in internal state β.

There are only two differences between eq 56 and the WCUB equation used previously.[22] The first is that the right-hand side involves a sum of collision terms involving each of the neutral gases. The other difference is that there is a reactive term on the left-hand side. Because reactions are assumed to be infrequent, this term can be dropped in all situations where the nonreactive term does not vanish. This means that the only time the reactive term is not dropped is when the equation of continuity is obtained by integrating the Boltzmann equation over all velocities. We thus obtain the rate equation of continuity, eq 13, where the two-body reaction rate coefficient is

$$k(\mathbf{r},t) = \sum_j x_j \sum_{\alpha,\beta} \int \int \left[\frac{f^{(\alpha)}(\mathbf{r},\mathbf{v},t)}{n(\mathbf{r},t)}\right]\left[\frac{F_j^{(\beta)}(\mathbf{V}_j)}{N_j}\right] \times Q_j^*(\alpha\beta;\, \epsilon_j)|\mathbf{v} - \mathbf{V}_j|\, \mathrm{d}\mathbf{V}_j\, \mathrm{d}v \quad (60)$$

To change eq 56 into equations governing moments of the ion velocity distribution function, we start with eq IV-15, i.e., with eq 15 of paper IV:[22]

$$f^{(\alpha)}(\mathbf{r},\mathbf{v},t) = n(\mathbf{r},t) f_0^{(\alpha)}(\mathbf{r},\mathbf{v},t) \sum_{l,m,n,o} c_{l,m,n,o}(\mathbf{r},t)\Psi_{l,m,n,o}(\mathbf{r},\mathbf{v},t,\epsilon^{(\alpha)}) \quad (61)$$

A series of systematic approximations for obtaining the expansion coefficients, $c_{l,m,n,o}(\mathbf{r},t)$, with increasing accuracy has been described previously.[22] The convergence of this series depends upon the particular choices made, and these in turn depend upon the symmetry and other properties of the experiment of interest.

3.1. Spherical-Basis Theory. The SB theory uses the choices

$$f_0^{(\alpha)(\mathrm{SB})}(\mathbf{r},\mathbf{v},t) = \frac{1}{Z}\left(\frac{m}{2\pi k_\mathrm{B} T_\mathrm{ion}(\mathbf{r},t)}\right)^{3/2} \exp(-W^2 - x^{(\alpha)}) \quad (62)$$

and

$$\Psi_{l,m,n,o}^{(\mathrm{SB})}(\mathbf{r},\mathbf{v},t) = W^l S_{l+1/2}^{(n)}(W^2) Y_l^m(\hat{\mathbf{W}}) R_o(x^{(\alpha)}) \quad (63)$$

where the only changes from the 2T theory are the introduction of the dimensionless internal energy

$$x^{(\alpha)} = \frac{\epsilon^{(\alpha)}}{k_\mathrm{B} T_\mathrm{int}(\mathbf{r},t)} \quad (64)$$

the WCU polynomials,[22,25] $R_0(x^{(\alpha)})$, and the ion partition function defined analogously to eq 59. The kinetic temperature, $T_\mathrm{ion}(\mathbf{r},t)$, of the ions is determined by constraining the solution of the Boltzmann kinetic equation that gives the $c_{l,m,n,o}(\mathbf{r},t)$ so that eq 21 applies. The internal temperature is similarly determined by the constraint that

$$\frac{\delta}{2} k_\mathrm{B} T_\mathrm{int}(\mathbf{r},t) = \sum_\alpha \int f^{(\alpha)}(\mathbf{r},\mathbf{v},t)[\epsilon^{(\alpha)}]\, \mathrm{d}\mathbf{v} \quad (65)$$

Here the factor, δ, that measures the number of active internal degrees of freedom of the ions has the value 2 if the ions are linear and a value of 3 or higher for more general molecular ions.

In first approximation, only four of the expansion coefficients in eq 61 are not equal to zero. We must have

$$c_{0,0,0,0}^{(\mathrm{SB})}(\mathbf{r},t) = (4\pi)^{1/2} \quad (66)$$

in order for the zero-order distribution function to be properly normalized. For the moments of the ion velocity to be correct in first approximation, we must have

$$c_{1,0,0,0}^{(\mathrm{SB})}(\mathbf{r},t) = 2\left(\frac{4\pi}{3}\right)^{1/2} \overline{W_z}(\mathbf{r},t) \quad (67)$$

and

$$c_{1,1,0,0}^{(\mathrm{SB})}(\mathbf{r},t) = -\left(\frac{2\pi}{3}\right)^{1/2} (\overline{W_y}(\mathbf{r},t) + i\, \overline{W_x}(\mathbf{r},t)) \quad (68)$$

$$c_{1,-1,0,0}^{(\mathrm{SB})}(\mathbf{r},t) = \left(\frac{2\pi}{3}\right)^{1/2} (\overline{W_y}(\mathbf{r},t) - i\, \overline{W_x}(\mathbf{r},t)) \quad (69)$$

We note in particular that constraining the kinetic temperature so that eq 21 holds means that we must have

$$c_{0,0,1,0}^{(\mathrm{SB})}(\mathbf{r},t) = 0 \quad (70)$$

while constraining the internal ion temperature so that eq 65 applies means that

$$c_{0,0,0,1}^{(\mathrm{SB})}(\mathbf{r},t) = 0 \quad (71)$$

These explicit expansion coefficients can be shown to yield the following first approximation to the reaction rate coefficient in the SB theory,

$$f^{(\alpha)}(\mathbf{r},\mathbf{v},t) = n(\mathbf{r},t) f_0^{(\mathrm{SB})}(\mathbf{r},\mathbf{v},t,x^{(\alpha)})[1 + 2\sum_u \overline{W_u}(\mathbf{r},t) W_u(\mathbf{r},\mathbf{v},t)] \quad (72)$$

This is the generalization to molecules of eq 27. Then eq 60 can be analyzed in the same manner as was used for eq 16 in the 2T theory. The SB result is identical in form with eq 34, with the identification that

$$Q_j^*(\epsilon) = \frac{1}{ZZ_j} \sum_{\alpha,\beta} \exp\left(-\frac{\epsilon^{(\alpha)}}{k_\mathrm{B} T_\mathrm{ion}(\mathbf{r},t)} - \frac{\epsilon_j^{(\beta)}}{k_\mathrm{B} T}\right) Q_j^*(\alpha,\beta;\, \epsilon) \quad (73)$$

There are therefore only two differences between the rate coefficient for molecular systems in the SB theory and those for atomic systems in the 2T theory. First, the total reaction cross-section must be computed by adding (with exponential weights) the state-specific cross-sections. Second, the presence of internal states influences the value of $T_\mathrm{ion}(\mathbf{r},t)$ and hence changes the numerical values of the reaction rate coefficients in ways that depend critically upon the experimental conditions and the particular ion, buffer, and reactive neutral being considered.

When the previous SB theory[22] is extended to gas mixtures, the differential equation governing any component ($u = x,y,z$) of the average velocity of the ion swarm in first approximation has the same form as eqs 35 and 36, but with $\xi_j(T_\mathrm{ion})$ replaced by $\xi_j^{(\mathrm{SB})}(T_\mathrm{ion})$, a generalized version of the momentum-transfer collision integral that is given by eq V-A5.[23] The moment equation for the ion temperature is

$$\frac{\partial}{\partial t} T_\mathrm{ion} - \frac{2q}{3k_\mathrm{B}} \mathbf{E}\cdot\bar{v} + \left[\sum_j x_j \frac{2m\xi_j^{(\mathrm{SB})}(T_\mathrm{ion})}{m + M_j}\right][T_\mathrm{ion} - T] + 2\sum_j x_j \xi_j(T_\mathrm{ion}) \Phi_j^{(\mathrm{SB})}(T_\mathrm{ion},T_\mathrm{int},T) T_j^{(\mathrm{eff})} = 0 \quad (74)$$

The dimensionless quantity $\Phi_j^{(\mathrm{SB})}(T_{\mathrm{ion}},T_{\mathrm{int}},T)$ is the dimensionless ratio of the collision integral for internal energy transfer to that for momentum transfer, as described in Appendix A of paper V.[23]

To complete the first approximation moment equations of the SB theory, we need the moment equation for T_{int}. This is given by eq V-4,[23] with the quantity $\Theta^{(\mathrm{SB})}(T_{\mathrm{ion}},T_{\mathrm{int}},T)$ given by summing eq V-A12[23] over each of the neutral gases in the mixture. This completes the first approximation of the SB theory, which will be discussed further in Section 4.

3.2. Cartesian-Basis Theory. The CB theory[22] is the generalization to molecules of the MT theory. It assumes that

$$f_0^{(\mathrm{CB})}(\mathbf{r},\mathbf{v},t,x^{(\alpha)}) = Z^{-1}\exp(-x^{(\alpha)})f_0^{(\mathrm{MT})}(\mathbf{r},\mathbf{v},t) \tag{75}$$

and

$$\Psi_{l,m,n,o}^{(\mathrm{CB})}(\mathbf{r},\mathbf{v},t,x^{(\alpha)}) = \Psi_{l,m,n}^{(\mathrm{MT})}(\mathbf{r},\mathbf{v},t)R_{\mathrm{o}}(x^{(\alpha)}) \tag{76}$$

Following the same procedure as with the MT theory, we find that the generalizations of eqs 43−46 are

$$c_{0,0,0,0}^{(\mathrm{CB})}(\mathbf{r},t) = 1 \tag{77}$$

and

$$c_{1,0,0,0}^{(\mathrm{CB})}(\mathbf{r},t) = \overline{W_x}(\mathbf{r},t) \tag{78}$$

$$c_{0,1,0,0}^{(\mathrm{CB})}(\mathbf{r},t) = \overline{W_y}(\mathbf{r},t) \tag{79}$$

$$c_{0,0,1,0}^{(\mathrm{CB})}(\mathbf{r},t) = \overline{W_z}(\mathbf{r},t) \tag{80}$$

All other expansion coefficients are zero in first approximation of the CB theory, so in this approximation eq 61 becomes

$$f^{(\alpha)}(\mathbf{r},\mathbf{v},t) = n(\mathbf{r},t)f_0^{(\mathrm{CB})}(\mathbf{r},\mathbf{v},t,x^{(\alpha)})[1 + 2\sum_u \overline{W_u}(\mathbf{r},t)W_u(\mathbf{r},\mathbf{v},t)] \tag{81}$$

which is the generalization of eq 48. Then eq 60 can be analyzed in the same manner as was used for eq 16 in the MT theory. The CB result is identical in form with eq 49, with the identification given in eq 73. Again, there are only two differences between the rate coefficient for molecular systems and those for atomic systems in the corresponding theory.

When the previous CB theory[22] is extended to gas mixtures, the differential equation governing any component of the average velocity of the ion swarm in first approximation has the same form as eqs 52 and 53, but with $\xi_{j,u}^{(\mathrm{MT})}(T_x,T_y,T_z)$ replaced by $\xi_{j,u}^{(\mathrm{CB})}(T_x,T_y,T_z,T_{\mathrm{int}},T)$, a generalized version of the momentum-transfer collision integral that is given by eq V-A7.[23] The moment equation for the ion temperature is

$$\frac{\partial}{\partial t}T_u - \frac{2q}{k_{\mathrm{B}}}\overline{E_u v_u} + \left[\sum_j x_j \frac{2m\xi_{j,u}^{(\mathrm{CB})}(T_x,T_y,T_z,T_{\mathrm{int}},T)}{m+M_j}\right][T_u - T] + 2\sum_j x_j \xi_{j,u}^{(\mathrm{CB})}(T_x,T_y,T_z,T_{\mathrm{int}},T)\Phi_{j,u}^{(\mathrm{CB})}(T_x,T_y,T_z,T_{\mathrm{int}},T)T_{j,u}^{(\mathrm{eff})} = 0 \tag{82}$$

The dimensionless quantity $\Phi_{j,u}^{(\mathrm{CB})}(T_x,T_y,T_z,T_{\mathrm{int}},T)$ includes the effects of energy partitioning and internal energy transfer, as described in Appendix A of paper V.[23]

To complete the first approximation moment equations of the CB theory, we need the moment equation for T_{int}. This is given by eq V-4, with the quantity $\Theta_u^{(\mathrm{CB})}(T_x,T_y,T_z,T_{\mathrm{int}},T)$ obtained by summing eq V-A11 over each of the neutral gases in the mixture.

4. Applications

We first consider the implications of our first approximation results for the ion velocity distribution function. We consider a quadrupole ion trap containing small amounts of singly charged atomic ions with mass $m = 100$ g/mol and a larger amount of neutral atoms with mass $M = 4$ g/mol, temperature $T = 300$ K, pressure $P = 0.001$ Torr, and dipole polarizability $\alpha = 0.2050$ Å^3. We assume that the ion-neutral interactions obey the Maxwell model of constant collision frequency, which for the values above is $\xi = 740.9$ s^{-1}, and that the 2T theory is adequate in this situation. We focus on the steady-state condition by assuming further that initial velocities in each direction have a Maxwellian distribution with zero average velocity and that the initial ion temperature is zero. The ion trap is assumed to operate at a frequency of 1.00 MHz (angular frequency $\Omega_{\mathrm{RF}} = 2\pi \times 10^6$ s^{-1}), and the magnitudes of the dc and ac fields are such that the usual trap parameters are $a_u = 0$ for $u = x,y,z$ and $q_z = -2q_x = -2q_y = 0.20$. We focus specifically on the point in the trap where $x = y = 0$ and $z = 0.005$ m. The results for $\overline{v_z}$ are shown as a curve in Figure 1 of our previous work;[21] because of the choices made here, the average ion velocities along the x and y axes are always zero and there is no exponentially damped term in the average ion velocity along the z axis. The results for the collision energy, $E_{\mathrm{c}} = 3k_{\mathrm{B}}T_j^{(\mathrm{eff})}(\mathbf{r},t)/2$, in the situation just described are plotted in Figure 2 of the previous paper, and these results can be converted to values of $T_{\mathrm{ion}}(\mathbf{r},t)$ using eq 32. Then eq 27 gives the velocity distribution functions shown in Figure 1.

The graphs show that symmetry around the v_x axis is retained; this is a result of our examining a position along the trap axis, z. They also show that the distribution moves outward, to larger v_z, as time goes on during a small portion of the first cycle of the RF trapping field. This is consistent with the $\overline{v_z}$ values we reported previously.[21] As time increases, the maximum of the distribution function decreases because it covers a larger range of $\overline{v_z}$ values. Although the volume under the curve also appears to decrease as time increases, this is artificial. The volume reduction arises because we have used only three dimensions rather than four because we know that the trap has $x-y$ symmetry. Hence as the distribution spreads along v_x, it also spreads along v_y, and volume appears to be lost.

The graphs contain regions of negative probability, but they are too small to be seen on Figure 1. Such unphysical results arise because the moment method focuses on the bulk of the distribution function, not the tails. Presumably, higher orders of approximation would gradually eliminate such regions, but such considerations are beyond the scope of this paper.

As an application of our results for reaction rate coefficients, we consider two models for the ion-neutral reaction cross-section. The first is a constant cross-section,

$$Q_{\mathrm{R}}^{*}(E_{\mathrm{rel}}) = \pi d^2 \tag{83}$$

which from eq 6 gives

$$k_{\mathrm{R}}^{(0)}(T_{\mathrm{R}}^{(\mathrm{eff})}) = \left(\frac{8k_{\mathrm{B}}T_{\mathrm{R}}^{(\mathrm{eff})}}{\pi\mu_{\mathrm{R}}}\right)^{1/2}\pi d^2 \tag{84}$$

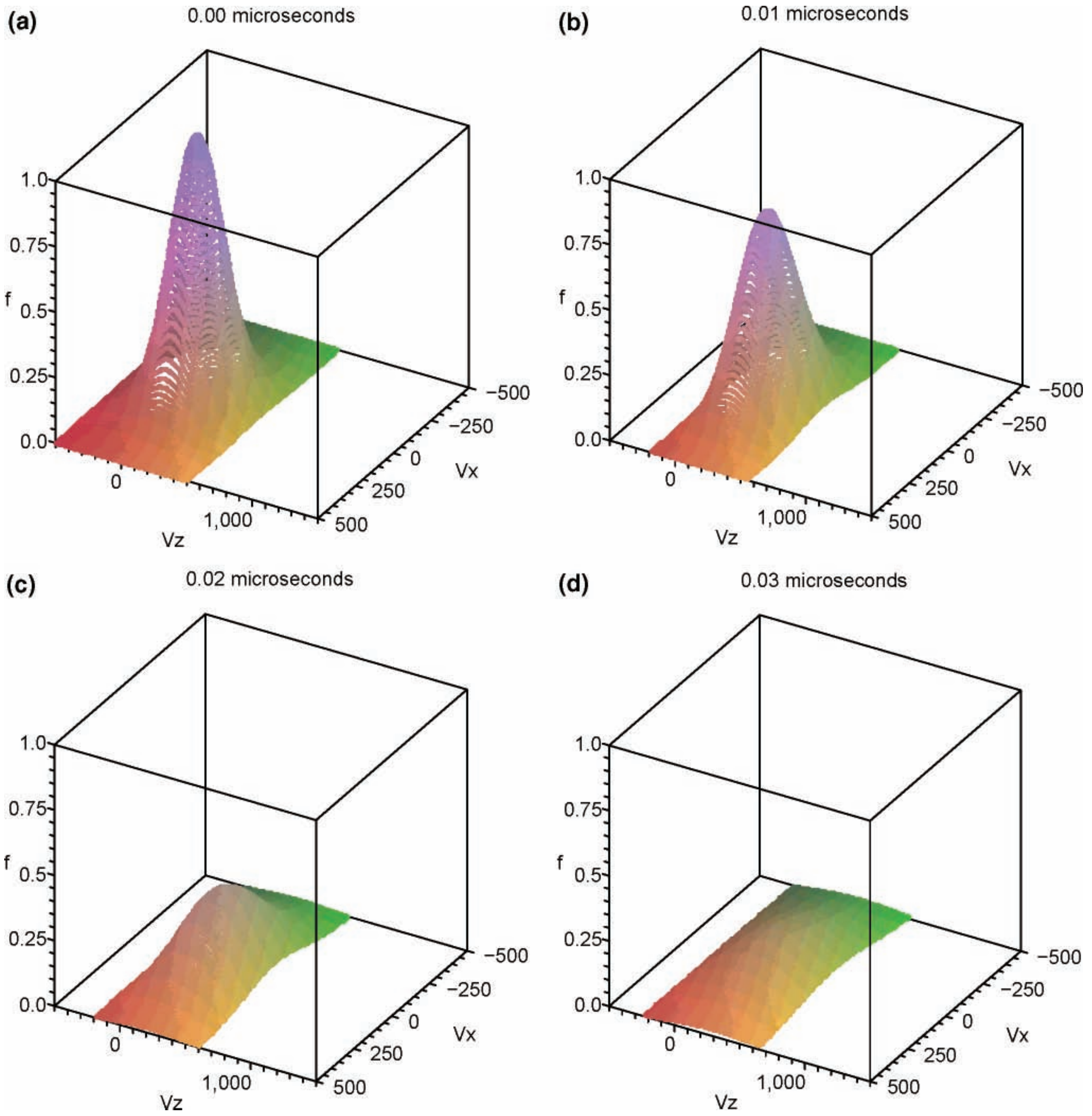

Figure 1. Three-dimensional plots of the four-dimensional surface representing the ion velocity distribution function in a quadrupole ion trap at selected times. The units for the velociities along the *x* and *z* directions are m s^{-1}. Panels a, b, c, and d correspond to $t = 0$, 0.01, 0.02, and 0.03 μs, respectively. The trap parameters and the details of the ion-neutral system are described in the text.

The second is similar to the Reid ramp model;[26] the reaction cross-section is 0 below some value E_a, while above this value, it is

$$Q_R^*(E_{rel}) = \pi d^2 \frac{E_{rel} - E_a}{E_{rel}} \qquad (85)$$

the corresponding expression for the reaction rate coefficient is

$$k_R^{(0)}(T_R^{(eff)}) = \left(\frac{8k_B T_R^{(eff)}}{\pi \mu_R}\right)^{1/2} \pi d^2 \exp\left(-\frac{E_a}{k_B T_R^{(eff)}}\right) \qquad (86)$$

Plots of the rate coefficients using values $\pi d^2 = 5.0 \times 10^{-20}$ m^2 and $E_a = 0.1$ eV are given in Figure 2.

For the Maxwell model, in which the ion-neutral interaction varies inversely with the fourth power of the separation between the collision partners, the collision frequency is constant and the momentum-transfer cross-section varies inversely with the square root of the energy. A similar model for the reaction cross-section is

$$Q^*(E_{rel}) = \pi q \left(\frac{2\alpha}{(4\pi\epsilon_0)E_{rel}}\right)^{1/2} \qquad (87)$$

where ϵ_0 is the electric constant. The corresponding reaction rate coefficient is then

$$k_R^{(0)}(T_R^{(eff)}) = q\left(\frac{\pi\alpha}{\epsilon_0 \mu_R}\right)^{1/2} \qquad (88)$$

i.e., it is independent of $T_R^{(eff)}$ and hence is not shown in Figure 2.

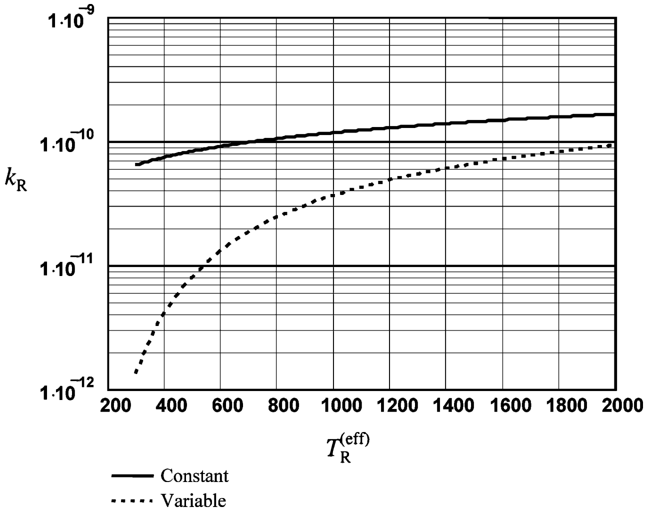

Figure 2. Reactive rate coefficient, k_R in units of cm^3 mol^{-1} s^{-1}, as a function of effective temperature, $T_R^{(eff)}$ in K, characterizing the reactive ion-neutral collisions. The models and their parameters are described in the text.

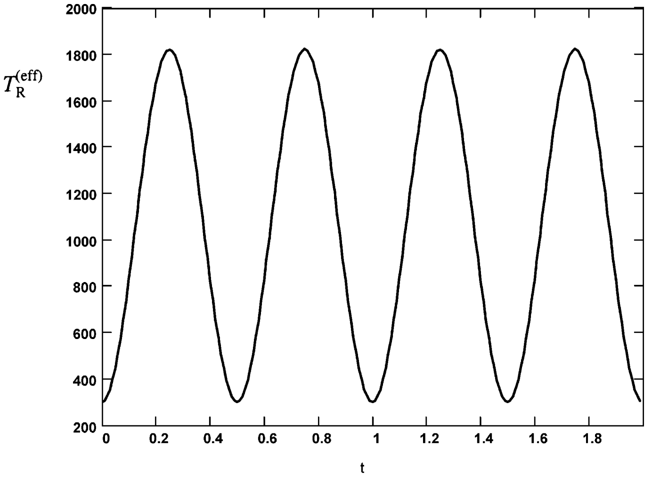

Figure 3. Variation with time, t, in μs, of the effective temperature, $T_R^{(eff)}$ in K, characterizing the reactive ion-neutral collisions. The trap parameters and the details of the ion-neutral system are the same as for Figure 1.

Because the rate coefficients generally vary with effective temperature, they will also vary with position and time in a quadrupole ion trap. Figure 3 shows the calculated time dependence of $T_R^{(eff)}$ over the first two cycles of the trapping RF signal when hard-sphere ion-neutral collisions are assumed. At the particular trap position used here, $T_R^{(eff)}$ varies from 300 to ∼1800 K during a time interval of 0.25 μs; $T_R^{(eff)}$ varies at twice the RF frequency because the ions absorb RF power during both the positive and negative phase of the signal.

Combining the data shown in Figures 2 and 3 with the three models for the reaction cross-section produces the plot for the time-dependent reaction rate coefficients in Figure 4 (note the logarithmic axis for the rate coefficients). There is a much larger variation in $k_R^{(0)}$ over time when Q^* is variable than when it is constant due to the large variation in $T_R^{(eff)}$ that occurs in the trap.

As a final note about reaction rate coefficients, the ion number density in a trap also shows a strong dependence upon time and position. The results in Figure 4 must then be convoluted with the results obtained previously[21] in order to determine the overall reaction rate in the entire trap. Such calculations will be reported in a future paper.

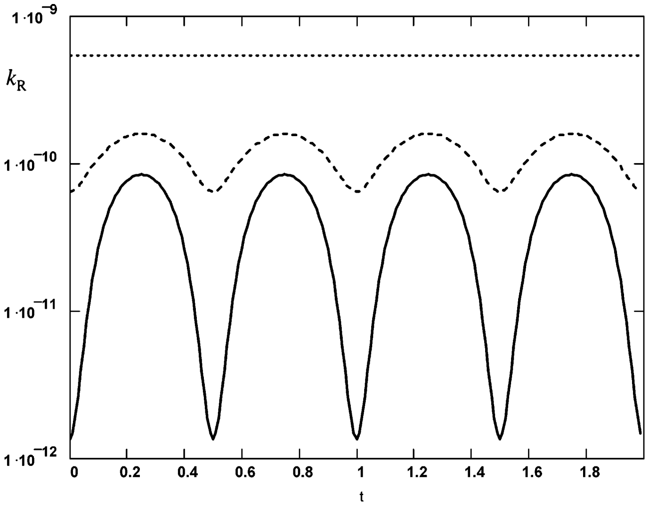

Figure 4. Variation with time, t, in μs, of the reaction cross-sections, k_R in units of cm^3 mol^{-1} s^{-1}, obtained by combining the results shown in Figures 2 and 3. From top to bottom, the curves represent the Maxwell, constant, and variable cross sections.

The calculated rate coefficients can be compared with absolute rate coefficients determined experimentally in a quadrupole ion trap. For the reaction of Br$^-$ with CH_3I, the measured reaction rate coefficient in a room-temperature ion trap[27] was 2.7×10^{-11} cm^3 mol^{-1} s^{-1}. Measurement in a flowing afterglow apparatus[28] at 298 K yielded a value of 2.89×10^{-11} cm^3 mol^{-1} s^{-1}. For reactions of $[Mo_2O_6(OH)]^-$ with a series of alcohols,[29] experimental measurements in the same instrument gave reaction rate coefficients ranging from 2.8×10^{-11} to 6.6×10^{-10} cm^3 mol^{-1} s^{-1}. The theoretical ion−molecule collision rates for these systems, calculated using the ADO method of Su and Bowers,[30] ranged from 1.22 to 1.40×10^{-9} cm^3 mol^{-1} s^{-1}.

5. Discussion

We have extended our recent moment theories for ion motion in traps and similar electrodynamic devices to include (infrequent) ion-neutral reactions in a gas mixture. The new result we find is that, in first approximation, ion−molecule reaction rate coefficients measured in traps and similar devices employing time- and position-dependent electric fields can be equated to thermal rate coefficients at an elevated temperature. In other words, rate coefficients appropriate to high temperatures in the absence of electric fields can be extracted from measurements at low temperatures and elevated electric field strengths even though the velocity distribution of the ions may differ substantially from a Maxwellian (atomic ions) or Maxwell−Boltzmann (molecular ions) distribution in the latter experiments.

Further, we have provided differential equations for the position- and time-dependent moments of ion velocity and energy, which are necessary to convert the actual experimental parameters to the corresponding elevated temperature. The differential equations of Section 2 can be applied to circumstances requiring either two-temperature or multitemperature theory for atomic species. In the case of molecular ions and neutrals, the corresponding differential equations obtained in Section 3 from the spherical-basis and Cartesian-basis theories also enable determination of the ion internal temperature. Furthermore, the expressions in both sections allow for mixtures of neutral gases in which more than one component is reactive.

We have shown that it is not necessary to determine the ion velocity distribution function in order to establish high-temperature thermal rate coefficients. Nevertheless, explicit expressions are provided herein for position- and time-dependent ion velocity distributions under all the aforementioned circumstances and in first approximation. The expressions require only knowledge of the average ion velocity and temperature (equivalently energy), which can be obtained as noted above from the solutions to the differential equations for the corresponding moments. It also should be noted that, in principle, our expressions enable the reaction cross-section to be ascertained from the measured rate coefficients by inverting the integral that relates the two quantities.

Acknowledgment. This material is based upon work supported by the National Science Foundation under grant no. CHE-0414241. The work carried out by DEG was sponsored by the Office of Basic Energy Sciences, U.S. Department of Energy. Oak Ridge National Laboratory is managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract no. DE-AC05-00OR22725.

References and Notes

(1) Albritton, D. L. *At. Data Nucl. Data Tables* **1978**, *22*, 1.

(2) Bogaerts, A.; Gijbels, R. *Phys. Rev. E* **2002**, *65*, 056402.

(3) Miller, T. M.; Friedman, J. F.; Williamson, J. S.; Viggiano A. A. *J. Chem. Phys.* **2006**, *124*, 144305.

(4) Atkins P.; De Paula, J. In *Physical Chemistry*, 8th ed.; Freeman: New York, 2006.

(5) Viggiano, A. A. *Phys. Chem. Chem. Phys.* **2006**, *8*, 2557.

(6) Wannier, G. H. *Bell Syst. Tech. J.* **1953**, *32*, 170.

(7) Viehland, L. A.; Lin, S. L.; Mason E. A. *Chem. Phys.* **1981**, *54* 341.

(8) Mason, E. A.; McDaniel, E. W. In *Transport Properties of Ions in Gases*; Wiley: New York, 1978; p 468.

(9) Albritton, D. L. In *Kinetics of Ion-Molecule Reactions*; Ausloos, P. Ed.; Plenum: New York, 1979, pp 119−142.

(10) Heimerl, J. M.; Johnsen, R.; Biondi, M. A. *J. Chem. Phys.* **1969**, *51*, 5041.

(11) Villinger, H.; Futrell, J. H.; Saxer, A.; Richter, R.; Lindinger, W. *J. Chem. Phys.* **1984**, *80*, 2543.

(12) Smith, D.; Spanel, P. *Mass Spectrom. Rev.* **2005**, *24*, 661.

(13) Fehsenfeld, F. C.; Ferguson, E. E.; Schmeltekopf, A. L. *J. Chem. Phys.* **1966**, *44*, 3022.

(14) Bierbaum, V. M., In *The Encyclopedia of Mass Spectrometry*; Armentrout, P. B., Ed.; Elsevier: Amsterdam, 2003; Vol. 1, pp 98−109.

(15) Viggiano, A. A., In *The Encyclopedia of Mass Spectrometry*; Armentrout, P. B., Ed.; Elsevier: Amsterdam, 2003; Vol. 1, pp 199−208.

(16) Viehland, L. A.; Mason, E. A. *J. Chem. Phys.* **1977**, *66*, 422.

(17) Lovejoy, E. R.; Wilson, R. R. *J. Phys. Chem. A* **1998**, *102*, 22309.

(18) Jackson, G. P.; King, F. L.; Goeringer, D. E.; Duckworth, D. C. *J. Phys. Chem. A* **2002**, *106*, 7788.

(19) Viehland, L. A.; Goeringer, D. E. *J. Phys. B* **2005**, *38*, 3987.

(20) Viehland, L. A.; Kabbe, E. A.; Dixit, V. V. *J. Phys. B* **2005**, *38*, 4011.

(21) Goeringer, D. E.; Viehland, L. A. *J. Phys. B* **2005**, *38*, 4027.

(22) Viehland, L. A.; Danailov, D. M.; Goeringer, D. E. *J. Phys. B* **2006**, *39*, 3993.

(23) Viehland, L. A.; Danailov, D. M.; Goeringer, D. E. *J. Phys. B* **2006**, *39*, 4015.

(24) Viehland, L. A.; Mason, E. A.; Whealton, J. H. *J. Phys. B* **1974**, *7*, 2433.

(25) Wang Chang, C. S.; Uhlenbeck, G. E.; De Boer, J. In *Studies in Statistical Mechanics*; De Boer, J., Uhlenbeck, G. E., Eds.; North-Holland: Amsterdam, 1964; Vol. 2.

(26) Reid, I. D. *Aust. J. Phys.* **1979**, *32*, 231.

(27) Waters, T.; O'Hair, R. A. J.; Wedd, A. G. *J. Am. Chem. Soc.* **2003**, *125*, 3384.

(28) Gronert, S.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1991**, *113*, 4009.

(29) Flores, A. E.; Gronert, S. *J. Am. Chem. Soc.* **1999**, *121*, 2627.

(30) Su, T.; Bowers, M. T. In *Gas-Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; p 83.