Multi-temperature moment theory of Ag$^+$ ion motion and reaction with D$_2$ in ion traps

Larry A. Viehland$^1$ and Douglas E. Goeringer$^2$

$^1$Division of Science, Chatham University, Pittsburgh, PA 15232-2813, USA
$^2$Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6131, USA

E-mail: viehland@chatham.edu

Abstract. A theoretical calculation is reported of the time and space dependence of the reaction rate coefficient in a stretched quadrupole ion trap. The system consists of Ag$^+$ ions moving in trace amounts through a dilute gas consisting primarily of He or Ar buffer gas, but with a small amount of a reactive neutral, D$_2$. These systems were chosen because there are available now accurate potential energy curves for Ag$^+$ ions interacting with He and Ar gas and because the cross section for Ag$^+$ reaction with D$_2$ is known over a wide range of collision energy.

1. Introduction

Moment theories of trace ion motion in traps and similar devices have been presented in a series of recent papers [1-5]. In first approximation, the multi-temperature theory [5] for atomic ion motion in atomic gases leads to two vector equations (equivalently, six scalar equations) that constitute a coupled set of ordinary differential equations. The solutions of these equations give the average ion speeds, $v_u(r,t)$, and the dimensionless collision energies, $e_u(r,t)$, defined below, along the three Cartesian axes ($u=x, y, z$) chosen to describe the apparatus, each as functions of position, $r$, and time, $t$. They therefore describe the ion motion in the apparatus in the absence of ion-neutral reactions. For example, numerical values for the $v_u(r,t)$ can be inserted into the equation of continuity, giving a partial differential equation that can be solved for the ion number density, $n(r,t)$, if we are given information about the initial conditions.

When there is a small amount of reactive neutral atoms or molecules mixed in with a much larger amount of non-reactive (buffer) atoms, the values of $v_u(r,t)$, $e_u(r,t)$ and $n(r,t)$ can be used [6] to determine the two-body, ion-neutral reaction rate coefficient, $k(r,t)$, at a particular position and time, or averaged over the entire apparatus and one or more cycles of the ac fields in the trap. The first purpose of the present paper is to make theoretical calculations of $v_u(r,t)$, $e_u(r,t)$ and $n(r,t)$ for Ag$^+$ ions moving in a stretched ion trap filled with He or Ar gas at 300 K, using the accurately known interaction potentials [7] for the HeAg$^+$ and ArAg$^+$ systems. The second purpose is to combine these values with the accurately known [8] integral cross section for Ag$^+$ reaction with D$_2$, thus determining the reaction rate coefficient.

2. Theory of the instrument

We assume that the quadrupole ion trap is cylindrically symmetric along the $z$ axis and that a time-dependent electric potential, $U+V \cos(\Omega_{RF} t)$, is applied to the ring electrode. Here $U$ is the amplitude of the dc component of the field and $V$ is the zero-to-peak amplitude of the ac component that has angular frequency $\Omega_{RF}$. We also assume that the hyperbolic end-cap electrodes are identical and arranged symmetrically, and that a time-dependent electric potential is applied between them in a dipolar fashion, i.e., so that one has $[U_D+V_D \cos(\Omega_{BF} t+\delta_D)]/2$ while the other has a negative value of exactly the same magnitude. Here $U_D$, $V_D$ and $\omega_D$ are the equivalents of $U$, $V$ and $\Omega_{RF}$, while $\delta_D$ is the phase shift that may
exist between the two ac components. For this arrangement, the total electric potential can be expressed [9] as a multipole expansion of the form

\[ \Phi(x,y,z,t) = [U + V \cos(\Omega_{RF}t)] \sum_{l=0}^{\infty} A^R_{2l} \left( \frac{r_{3D}}{r_0} \right)^{2l} P_{2l} \left( \frac{x}{r_{3D}} \right) 
+ \frac{1}{2} \left[ U_D + V_D \cos(\omega_D t + \delta_D) \right] \sum_{l=0}^{\infty} A^D_{2l+1} \left( \frac{r_{3D}}{r_0} \right)^{2l+1} P_{2l+1} \left( \frac{z}{r_{3D}} \right), \]  

(1)

where \( r_0 \) is the internal radius of the trap rings, \( P_l(x) \) is the Legendre polynomial of order \( l \) and argument \( x \), and

\[ r_{3D}^2 = x^2 + y^2 + z^2. \]  

(2)

is the distance in three-dimensional (Cartesian) space. The dimensionless expansion coefficients, \( A_l \), have superscripts \( R \) and \( D \) to serve as reminders that the terms involve the ring and dipole (endcap) potentials, respectively. Their values have been given through \( l=6 \) for many different trap geometries [5,9,13].

It is important to note that eq. (1) depends only upon \( r \) and \( z \) in cylindrical polar coordinates \((r,\theta,z)\), where \( r \) is the two-dimensional distance in the \( x-y \) plane. We assume that the ion trap is symmetric along the \( z \) axis about a point \((z=0)\) midway between the endcaps. Hence we will hereafter use cylindrical polar rather than Cartesian coordinates, and we need be concerned only with the region \( 0 \leq r \leq \infty \) and \( 0 \leq z \leq \infty \). In practice, of course, the ions do not reach infinity along either axis; indeed, they are generally much closer to the point where both \( r \) and \( z \) are zero than to any of the electrodes that enclose them.

Here and in each of the other sections of this paper, it is important to give a careful discussion of the possible errors. We will truncate eq. (1) so that only the first six \( A_l \) are non-zero. As explained below, we have repeated our calculations while also setting \( A_5 = A_6 = 0 \). The differences between the theoretical values of the average reaction rate coefficient are negligible, which leads us to believe that keeping only terms through \( A_6 \) should lead to no substantial error. There is one caveat to this conclusion, however. While it is entirely feasible to compute the theoretical values of \( A_l \) to as high a value of \( l \) as may be desired, there is no easy way to assess how well the real ion trap matches eq. (1) with the values assumed for the first six \( A_l \). Overall, we estimate that the errors due to our use of the truncated eq. (1) are less than 0.9%.

### 3. First-order moment theory

As shown in our previous work [5], the moment equations for the components of the average ion velocity can be cast into forms similar to those ordinarily employed [14] in trap studies of the motion of a single ion. These ordinary differential equations for the average speeds in the radial \((u=r)\) and axial \((u=z)\) directions in cylindrical polar coordinates are

\[ \frac{d}{dt} u + \frac{\alpha^R_{EF}}{4} \left[ \tilde{a}_u - 2 \tilde{d}_u \cos(\Omega_{RF}t) \right] u + \epsilon^{(MT)} u = 0, \]

(3)

where
and where, for simplicity, we have not explicitly indicated the position and time dependence of the $v_u(r,t)$. The quantities $\tilde{a}_u$ and $\tilde{q}_u$ are modifications [13] of the usual $a_u$ and $q_u$ that are dimensionless versions of $U$ and $V$ for ion traps. The modifications are made using the $A_i$, and they account for the stretched or otherwise non-ideal nature of the traps. The quantities $\tilde{b}_u$ and $\tilde{d}_u$, defined previously [13], indicate how the presence of a dipole potential between the endcaps modifies the differential equations.

Finally, the collision frequency for momentum transfer along the $u$ axis, $\xi_u^{(\text{MT})}$, depends upon two effective temperatures, $T_r^{(\text{eff})}$ and $T_z^{(\text{eff})}$, as noted below.

It is convenient to introduce the dimensionless effective temperatures,

$$
\epsilon_u = \frac{T_u^{(\text{eff})}(r,t)}{3T},
$$

which are implicitly dependent upon $r$ and $t$. The factor of 3 is introduced into eq. (6) so that, when the ion temperatures are identical, $2\epsilon_r + \epsilon_z$ becomes equal to the ratio of the average ion energy (independent of direction) to the thermal energy, $3k_B T/2$, where $T$ is the gas temperature and $k_B$ is Boltzmann’s constant. Since $\xi_u^{(\text{MT})}$ depends upon $T_r^{(\text{eff})}(r,t)$ and $T_z^{(\text{eff})}(r,t)$, the $\epsilon_u$ can also be considered to be dimensionless collision energies.

The moment equations governing the $\epsilon_u$ are [5]

$$
\frac{d}{dt} \epsilon_u + \frac{\mu \Omega_R^2}{6k_B T} [\tilde{a}_u - 2\tilde{q}_u \cos(\Omega_R t)] \nu u_u
$$

$$
+ \frac{\mu \Omega_R^2}{6k_B T} [\tilde{b}_u - 2\tilde{d}_u \cos(\omega_D t + \delta_D)] f u_u
$$

$$
+ 2\mu \xi_u^{(\text{MT})} \left( \epsilon_u - \frac{1}{3} + \frac{M \Phi_u^{(\text{MT})}}{m} - \epsilon_u \right) = 0.
$$

The dimensionless ratios $\Phi_u^{(\text{MT})}$ provide for energy partitioning [15] in the multi-temperature theory, as described below and in the appendix of a previous paper [5]. Like the collision frequencies, they depend upon $T_r^{(\text{eff})}$ and $T_z^{(\text{eff})}$.

Eqs. (3) and (7) are valid only in the first approximation of the multi-temperature moment theory [5]. Although it is possible to extend the theory to second order or beyond, this task is beyond the scope of this paper. For now it suffices to note that momentum-transfer theory [16] and the first approximation of the three-temperature kinetic theory [17] of gaseous ion transport in drift tubes with electrostatic fields are generally accurate within 10%, but for ion/neutral mass ratios as high as for Ag+ in He, they are accurate within 3% [18]. Hence we tentatively estimate that our use of eqs. (3) and (7) should lead to results accurate within 3% for the calculations with He and within 5% for those with Ar. These potential errors are large enough to encompass the small errors that arise from using 100 steps, covering one full cycle of the AC field, to solve eqs. (3) and (7) by a fourth-order Runge-Kutta method [19].
4. Collision frequencies

The collision frequency for momentum transfer in the multi-temperature theory is [5]

\[ \xi_0^{(MT)} = \frac{8N\mu}{3m} \left( \frac{2k_BT}{\pi\mu} \right)^{\frac{1}{2}} < \gamma_{\mu}^2 >^{(1)}, \]  

(8)

where \( N \) is the gas number density, \( \mu \) is the ion-buffer reduced mass, and \( m \) is the ion mass. The quantity \( \Phi_u^{(MT)} \) is

\[ \Phi_u^{(MT)} = \frac{3\varepsilon_u <\gamma_{\mu}^2>^{(2)} - 2\varepsilon_r <\gamma_{\mu}^2>^{(1)} - \varepsilon_z <\gamma_{\mu}^2>^{(2)}}{6\varepsilon_u <\gamma_{\mu}^2>^{(1)}}. \]  

(9)

Here the generalized collision integrals, \( <\gamma_{\mu}^2>^{(l)} \), are energy averages of the usual [20] transport cross sections, \( Q^{(l)} \). When cylindrical polar coordinates are used to take advantage of the cylindrical symmetry of the apparatus, the general expression [5] reduces to

\[ < A >^{(l)} = 3\sqrt{3} \int_0^\infty d\gamma_r \gamma_r \int_0^\infty d\gamma_z \exp(-\gamma_r^2 - \gamma_z^2) A \]

\[ \times Q^{(l)}(3k_BT[\gamma_r^2 \varepsilon_r + \gamma_z^2 \varepsilon_z]) [\gamma_r^2 \varepsilon_r + \gamma_z^2 \varepsilon_z]^{\frac{3}{2}} \]  

(10)

for any quantity, \( A \), that is an even function of \( r \) and/or \( z \). [This equation also corrects important errors in eq. A.4 of [5], due to neglect of the factor of 3 in eq. (6).]

We have used computer program QVALUES [21, 22] to calculate the transport cross sections with a precision of 0.01\% for relative kinetic energies between \( 10^{-9} \) and 10 hartree, using highly accurate, \textit{ab initio}, interaction potentials [7] for HeAg\(^+\) and ArAg\(^+\). It is possible that these potentials may still have room for improvement and it is necessary, moreover, to evaluate the generalized collision integrals by numerical quadrature of the double integrals in eq. (10). Nevertheless, we do not believe that the collision integrals, and hence \( \xi_u \) and \( \Phi_u^{(MT)} \), are in error by more than 0.1\%.

5. Ion number density

Since we obtain numerical rather than analytical values of \( \nabla_u \) by solving eq. (3), the equation of continuity [1],

\[ \frac{\partial n}{\partial t} + \nabla \cdot (n\mathbf{v}) = 0, \]  

(11)

also must be solved numerically to obtain the ion number density at any position in the apparatus and at any time. Since cylindrical symmetry ensures that neither \( n \) nor \( \mathbf{v} \) depends upon \( \theta \), eq. (11) may be written as

\[ \frac{\partial n}{\partial t} + \frac{\partial n\mathbf{v}_r}{\partial r} + \frac{\partial n\mathbf{v}_z}{\partial z} = 0. \]  

(12)

We have extended our previous computer program [5] to encompass the solution of eq. (12) by the forward-time, forward-space version of the finite difference method [19]. This requires knowledge
of \( n(r,z,t) \) at \( t=0 \). Assuming that no special experimental techniques have been implemented, this quantity may be assumed to be normally distributed along both \( r \) and \( z \). Thus,

\[
n(r, z, 0) = \left( \frac{2}{\pi} \right)^{1/2} \frac{n_0}{\sigma_r \sigma_z} \exp \left( -\frac{r^2}{2\sigma_r^2} - \frac{z^2}{2\sigma_z^2} \right).
\]  

The constants in eq. (13) ensure that the total ion number in the entire apparatus is \( n_0 \), since

\[
\int_0^\infty dr \int_0^\infty dz \, n(r, z, 0) = n_0.
\]  

The accuracy of the numerical solution of eq. (13) depends primarily upon the grid size used to cover the positions in the apparatus. In one set of calculations reported below, we used 11 points to cover \( r \) values from 0 to four times the standard deviation, \( \sigma_r \), assumed for the ion number density along this axis and, similarly, 11 points along \( z \). The results appeared generally to be of fair quality, but there were some points at which unphysical results were achieved, i.e., the number density was negative. The curves were of higher quality when we instead used 26 points along each axis, and the unphysical regions occurred at larger values of \( r \) and \( z \), where the curves oscillate around 0. A numerical estimate that these effects cause an error of no more than 4\% in the reaction rate coefficient is discussed in the next section.

6. Reaction rate coefficient

The multi-temperature expression for the rate coefficient has been given previously [6]. When there is only one reactive neutral species (R) and when the ion trap has cylindrical symmetry, this equation can be put into a form similar to that above for the non-reactive collisions. Thus,

\[
k(r, z, t) = \frac{4}{3} \left( \frac{2k_BT}{\pi \mu_R} \right)^{1/2} <A^{(*)}>^2,
\]

where

\[
<A^{(*)}> = \int_0^\infty d\gamma_r \gamma_r \int_0^\infty d\gamma_z \exp(-\gamma_r^2 - \gamma_z^2) A
\]

\[
\times Q^*_R(k_BT[\gamma_r^2 \epsilon^*_r + \gamma_z^2 \epsilon^*_z]) [\gamma_r^2 \epsilon^*_r + \gamma_z^2 \epsilon^*_z]^{1/2}
\]

and where

\[
\epsilon^*_u = \frac{m}{m+M} + \frac{M_R}{m+M_R} \frac{m+M}{M} \left[ 3\epsilon_u - \frac{m}{m+M} \right]
\]

In these equations, \( M_R \) is the mass of the reactive neutral, \( \mu_R \) is the reduced mass of the ion-reactive neutral pair, and \( Q^*_R \) is the energy-dependent, integral cross section for reaction.

Eqs. (15)-(17) allow the reaction rate coefficient at a particular position and time to be calculated from the results obtained by solving eqs. (3) and (7). From these results, it is, in turn, possible to compute the average reaction rate coefficient,

\[
\bar{k} = \frac{1}{n_0} \int_0^\infty dr \int_0^\infty dz \, k(r, z, t) \, n(r, z, t).
\]
However, values of $n(r,z,t)/n_0$ are obtained at a finite set of discrete values of $r$, $z$ and $t$, so it is important when converting the integrals in eq. (18) into sums to multiply by the appropriate volume element, $r \Delta r \Delta z \Delta t$, and to avoid the accumulation of round-off errors.

7. Calculations

We applied the theory above to two situations where Ag$^+$ ions moved through a non-reactive buffer gas, either helium or argon. In each case, a mole fraction of 0.1% D$_2$ was assumed to be present. The ion trap was assumed to be a Finnigan LCQ™ operating under the conditions given in table 1, where initial conditions and other parameters are also collected. We will discuss in detail only the results obtained when the buffer gas was argon and when 100 values along $t$ and 11 values along $r$ and $z$ were used.

| Parameters | Helium | Argon |
|------------|--------|-------|
| $r_0$, in mm | 0.707 | 0.707 |
| $z_0$, in mm | 0.783 | 0.783 |
| $A^r_0$ | 0.2151 | 0.2151 |
| $A^z_0$ | -0.5744 | -0.5744 |
| $A^\theta_0$ | 0.0978 | 0.0978 |
| $A^\phi_0$ | -0.0044 | -0.0044 |
| $A^\delta_0$ | -0.0225 | -0.0225 |
| $A^\phi_0$ | -0.0021 | -0.0021 |
| $\Omega_{bf}$ in MHz | 0.760 | 1.000 |
| $\omega_p$ in MHz | 0.110 | 0.000 |
| $\delta_p$ | 0.000 | 0.000 |
| $a_z = -2a_r$ | -0.050 | 0.000 |
| $q_z = -2q_r$ | 0.400 | 0.800 |
| $b_z = -2b_r$ | 0.000 | 0.000 |
| $d_z = -2d_r$ | 0.000459 | 0.000 |
| Range of $r$, in mm | 0-2.84 | 0-2.84 |
| Number of $r$ values | 11 or 26 | 11 or 26 |
| Range of $z$, in mm | 0-1.42 | 0-1.42 |
| Number of $z$ values | 11 or 26 | 11 or 26 |
| Range of $t$, in $\mu$s | 0-1.00 | 0-1.00 |
| Number of $t$ values | 101 | 100 |
| $v_x(r,z,t = 0)$, in m/s | 152.753 | 152.753 |
| $v_y(r,z,t = 0)$, in m/s | 152.753 | 152.753 |
| $3e_x(r,z,t = 0)$ | 1.000 | 1.000 |
| $3e_y(r,z,t = 0)$ | 1.000 | 1.000 |
| $\sigma_r$, in mm | 0.710 | 0.710 |
| $\sigma_z$, in mm | 0.355 | 0.355 |

Figure 1 shows the average Ag$^+$ speed along the $z$ axis as a function of time, at four values of the position along $z$ and for two values of position along $r$. Although the curves and dots do not have identical values, $v_z(r,z,t)$ is essentially independent of $r$ but a strong function of $z$. This is consistent with eq. (3) when $u=z$, where the differential equation has a term directly proportional to $z$ but where $r$ can affect the results only by its effect upon the ion
temperatures, which in turn affect the collision frequencies. Note from Figure 1 that one cycle of $v_z(r,z,t)$ occurs in the same amount of time that it takes for a full cycle of the ac field.

![Figure 1](image)

**Figure 1**: Average Ag$^+$ speed, in m/s, along the trap axis (z direction) as a function of time, in $\mu$s, when the trap contains Ar at 300 K and 0.01 torr. In order of increasing amplitude, the results correspond to $z=0, 0.142, 0.284$ and 0.426 mm from the midpoint of the trap. The curves correspond to values at $r=0$ mm from the trap midpoint, while the dots correspond to $r=0.852$ mm.

Figure 2 shows the average ion speed along the r axis as a function of time. Here we see that $v_r(r,z,t)$ is essentially independent of $z$ but a strong function of $r$. Again, this is consistent with eq. (3). It is interesting to note, however, the phase difference between Figures 1 and 2. The ac field along $z$ increases during the first part of the cycle, so $v_z(r,z,t)$ is in phase with this field but $v_r(r,z,t)$ is out of phase. This is usual for quadrupole ion traps, and results from the fact that the sum of the dimensionless field terms (in this case, $q_z + 2q_r$) must be zero.

The effective ion temperatures are shown in Figures 3 and 4. As with the average ion speeds, $T_z^{(eff)}(r,z,t)$ is essentially independent of $r$ but a strong function of $z$, while $T_r^{(eff)}(r,z,t)$ is essentially independent of $z$ but a strong function of $r$. Note, however, that two cycles of these temperatures occur during one cycle of the ac field, a result of the fact that the ion temperature increases when the ion speed increases, whether this increase means more positive or more negative values of the speed. The difference in the magnitude of the two peaks shown in each figure is a result of starting the calculations with initial speeds that are positive along both $r$ and $z$ (see table 1).
Figure 2: Average $\text{Ag}^+$ speed, in m/s, along the $r$ direction as a function of time, in $\mu$s, when the trap contains Ar at 300 K and 0.01 torr. In order of increasing amplitude, the results correspond to $r=0, 0.284, 0.568$ and $0.852$ mm from the midpoint of the trap. The curves correspond to values at $z=0$ mm from the trap midpoint, while the dots correspond to $r=0.994$ mm.

Figure 3: Same as Fig. 1, for the effective ion temperature, in K, along $z$. 
Figure 4: Same as Fig. 2, for the effective ion temperature, in K, along $r$.

The results in Figures 1-4 are consistent with similar results obtained previously [5]. The fact that there is little variation in the average speed or collision energy along either axis in the trap is why the device does indeed trap ions. When a small field is applied in a dipolar fashion to the end-caps, there is a special, “resonance” value of the dipole field that causes ion ejection. What these figures suggest, and what we have shown more conclusively with previous calculations [5], is that a dipole field acts to move ions off the axes, where they encounter large fields due to the ring electrodes, move to higher average speeds and energies, and (when there is a proper match between the dipole and ring fields) are ejected. In short, this is not a true resonance effect.

Completely new results are the effective reaction temperatures shown in Figures 5 and 6. These quantities are related to the $e_u^*$ defined by eq. (17) or, equivalently, they are defined by the equation

$$T_{R,u}^{(eff)}(r,z,t) = \frac{mT + M_R T_u(r,z,t)}{m + M_R}.$$  \hspace{1cm} (19)

The effective reaction temperatures characterize the relative kinetic energies between the ions and reactive neutral molecules. Therefore, Figures 5 and 6 show that few Ag+-D$_2$ collisions will have energies above the reaction threshold of 1.89 eV (equivalent to 2.19$\times$10$^4$ K). The reaction rate coefficient will therefore turn out to be quite small.
Figure 5: Same as Figs. 1 and 3, for the effective reaction temperature, in K, along z.

Figure 6: Same as Figs. 2 and 4, for the effective reaction temperature, in K, along r.
Figure 7 shows the ion number density as a function of time and position along \( z \), for a set of values of \( r \). The values plotted are relative values for points in a particular grid of 11x11 values that characterize the distances along \( r \) and \( z \) between 0 and four times the standard deviations given in table 1.

![Figure 7: Normalized ion number density, \( n/n_0 \), as a function of \( z \), in mm, at \( r=0.852 \) mm. The top set of points corresponds to \( t=0.99 \) \( \mu s \). The other sets correspond, in order of decreasing amplitude, to \( t=0, 0.1, 0.2 \) and \( 0.3 \) \( \mu s \).](image)

We have made calculations similar to those shown in Figure 7 using a 26x26 grid. The \( n/n_0 \) values have smaller magnitudes due to the smaller volume element in three-dimensional space that each value represents. More significantly, the unphysical oscillations have smaller amplitudes that occur only at larger values of \( z \) and \( t \). In future work it will be important to choose the number of time steps (100 here) and the size of the grid in \( r-z \) space carefully, using values small enough to keep the calculation time feasible but large enough that the influence of numerical inaccuracies on the final results is negligible.

Note from Figure 7 that the ion density has a maximum at \( z=0 \), i.e. in the middle of the trap. A similar plot of \( n/n_0 \) as a function of \( t \) and \( r \) but at constant \( z \) appears to show that the maximum ion number density lies some distance away from the radial axis of the trap. This is artificial and is a result of our use of cylindrical polar coordinates, where the volume element is \( r\Delta r\Delta z \).

An important feature of Figure 7 is that it shows that the ion number density at the end of one cycle of the ac field is quite different than at \( t=0 \), even though it still appears to be a normal distribution. This means that the standard deviations shown in Table 1 are inconsistent with the other parameters, in the sense that they do not describe the steady-state situation corresponding to the other parameters. Future work will involve repeating these calculations.
until standard deviations are found that do bring the ion number density after one cycle back to the normal distribution assumed to be present at \( t=0 \). Repetitive calculations of this type will be more efficient than solving the moment equations over a large enough number of cycles that steady-state is achieved.

Figures 8 and 9 show the results obtained from eq. (12) for the reaction rate coefficient. Note that the curves and points do not agree, unlike was the case in Figures 1-6. This means that the variation of \( k(r, z, t) \) along \( z \) is affected by the value of \( r \), and vice versa.

![Figure 8](image)

**Figure 8**: Same as Figs. 1, 3 and 5, for the rate coefficient for the reaction of \( \text{Ag}^+ \) ions with \( \text{D}_2 \).

It is a straightforward task to average the results illustrated in Figures 7-9 to obtain the weighted average of \( k(r, z, t) \) over all values of \( r \) and \( z \) and over one cycle of the ac field:

\[
\bar{k} = \frac{1}{\tau} \int_0^\tau \left[ \int_0^{r_{\max}} \int_0^{z_{\max}} n(r, z, t)k(r, z, t)rdrdz \right] dt.
\]  

(20)

Here \( \tau \) is one period of the ac field, and the weighting accounts for the different ion number densities at these values of \( r \), \( z \) and \( t \).

Our final result is that \( \bar{k}=8.3338 \times 10^{-15} \text{ cm}^3/\text{s} \) when the buffer gas is argon, when we use 100 steps to cover the time \( \tau \), and when we use a 11x11 grid to cover the \( r-z \) plane. When we changed to a 26x26 grid but left all other conditions the same, we found that \( \bar{k}=8.0977 \times 10^{-15} \text{ cm}^3/\text{s} \); the difference is 2.9%. As indicated previously, we repeated the argon calculations with \( A_5=A_6=0 \), in order to assess the effect of possible errors in the theoretical description of the instrument; the resulting values were \( 8.3317 \times 10^{-15} \text{ cm}^3/\text{s} \) for a 11x11 grid and \( 8.0979 \times 10^{-15} \text{ cm}^3/\text{s} \).
cm$^3$/s for a 26x26 grid; the differences between these values and those obtained using the values of $A_5$ and $A_6$ in table 1 are negligible.

Figure 9: Same as Figs. 2, 4 and 6, for the rate coefficient for the reaction of Ag$^+$ ions with D$_2$.

With a helium buffer gas, we found that $\bar{k}=4.7847 \times 10^{-15}$ cm$^3$/s using a grid of 11x11. This value is substantially smaller than in argon, primarily because the value of $q_x$ was much smaller. Somewhat smaller effects are due to the different values of the other parameters in table 1, the much larger ion-neutral mass ratio in helium, and the differences in the ion-neutral interaction potentials. In future work we will explore how variations in the dipole fields (e.g., the values of $b_x$ and $d_x$) may lead to a resonance that significantly increases the reaction rate coefficient.

8. Discussion

We have calculated the time and space dependences of the reaction rate coefficient for Ag$^+$ ions reacting with D$_2$ in a quadrupole ion trap filled with He or Ar. We have also determined the average of the rate coefficient over all positions in the trap and over one full cycle of the ac field. The values of $\bar{k}$ are smaller than the usual lower limit [23] for trap studies, i.e. $1 \times 10^{-13}$ cm$^3$/s. This means that reaction times longer than the usual 50 s will need to be used in future measurements of this rate coefficient in a quadrupole ion trap.

The total error in our calculations is estimated to be no more than 7% when the buffer gas is helium, and no more than 9% for argon. This is composed of: 0.9% for possible differences between the real ion trap and the description provided by eq. (1) and the values assumed for the first six $A_i$; 3% for helium and 5% for argon, due to the use of the first-order
moment theory and the use of 100 time steps to cover one full cycle of the ac field; 0.1% for the numerical calculation of the collision frequencies from the ion-neutral interaction potential; and 3% due to the use of a 26x26 grid in r and z and the numerical evaluation of eq. (16).

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References

[1] Viehland L A and Goeringer D E 2005 J. Phys. B: At. Mol. Opt. Phys. 38 2987
[2] Viehland L A, Kabbe E A and Dixit V V 2005 J. Phys. B: At. Mol. Opt. Phys. 38 4011
[3] Goeringer D E and Viehland L A (2005) J. Phys. B: At. Mol. Opt. Phys. 38 4027
[4] Viehland L A, Danailov D M and Goeringer D E 2006 J. Phys. B: At. Mol. Opt. Phys. 39 3993
[5] Viehland L A, Danailov D M and Goeringer D E 2006 J. Phys. B: At. Mol. Opt. Phys. 39 4015
[6] Viehland L A, Danailov D M and Goeringer D E 2007 J. Phys. Chem. A 111 2820
[7] Yousef A, Shrestha S, Viehland L A, Lee E P F, Gray B R, Ayles V L, Wright T G and Breckenridge W H 2007 J. Chem. Phys. 127 134302
[8] Chen Y-M, Elkind J L and Armentrout P B 1995 J. Phys. Chem. 99 10438
[9] Plass W R 2000 Int. J. Mass Spectrom. 202 175
[10] Beaty E C 1986 Phys. Rev. A 33 3645
[11] Wang Y and Franzen J 1994 Int. J. Mass Spectrom. Ion Proc. 132 155
[12] Plass W R 2001, Ph. D. Thesis, Justus-Liebig University, Giessen, Germany
[13] Goeringer D E, Viehland L A and Danailov D M 2006 J. Am. Soc. Mass Spectrom. 17 889
[14] March R E and Todd J F J 1995 "Practical aspects of ion trap mass spectrometry", Fundamentals of Ion Trap Mass Spectrometry, vol. 1 (Boca Raton, Florida: CRC Press).
[15] Viehland L A, Mason E A and Wheaton J H 1974 J. Phys. B 7 2433
[16] Robson R E 2006 Introductory Transport Theory for Charged Particles in Gases (Singapore: World Scientific)
[17] Lin S L, Viehland L A and Mason E A 1979 Chem. Phys. 37 411
[18] Viehland L A and Lin S L 1979 Chem. Phys. 43 135
[19] Asaithambi N S 1995 Numerical Analysis: Theory and Practice (Fort Worth: Saunders)
[20] Mason E A and McDaniel E W 1978 Transport Properties of Ions in Gases (New York: Wiley) p. 468
[21] Viehland L A 1982 Chem. Phys. 70 149
[22] Viehland L A 1984 Chem. Phys. 85 291
[23] Gronert S 2005 Mass Spectrom. Rev. 24 100