Dependence of Zero-field Ion Mobilities on Well Depth and Minimum Position in the Ion–Neutral Interaction Potential

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Abstract

The dependence, at fixed temperature, of the zero-field ion mobility on well depth ϵ and minimum position r_m in the ion–neutral interaction potential is explored. For large values of r_m the mobility is very sensitive to small changes in ϵ, but at small r_m the mobility varies only slightly from the Langevin value.

1. Introduction

The interaction of an atomic ion and a neutral atom at short–medium range is either attractive or repulsive. If the interaction is attractive, there will be a definite minimum in the potential energy curve $V(r)$. At long range the interaction energy is dominated by the attractive ion-induced dipole term $\frac{1}{2}\alpha^2 q^2/4\pi\epsilon_0\, r_m^4$. At very short range the potential is always repulsive. Thus, even for a repulsive interaction, there will always be a minimum in the potential energy curve. We have found previously (Harland *et al.* 1986; Simpson *et al.* 1987) that the calculated low-field ion mobility can be very sensitive to small changes in the magnitude of a long range van der Waals attractive well in the interaction potential. To investigate this behaviour further we have performed low-field two-temperature theory mobility calculations using a number of different hypothetical potentials. We have found that for certain values of the well depth ϵ and minimum position r_m the interaction potential need only be changed slightly to effect large changes in the calculated mobility, but this sensitivity varies significantly over the ranges of r_m and ϵ considered.

2. Theory and Method

Given $V(r)$, it is possible to calculate the drift velocity v_d and the ion mobility reduced to STP, K_0, as a function of electric field strength E/N (Mason and Schamp 1958):

$$K_0 = \frac{v_d}{E} = \frac{3q}{8N_0}\left(\frac{\pi}{2\mu k_B\, T_{\text{eff}}}\right)^{\frac{1}{2}}\frac{1+\alpha'}{\Omega^{(1,1)}(T_{\text{eff}})}, \tag{1}$$

where N_0 is the particle density reduced to STP, q is the charge on an electron and

k_B is Boltzmann's constant. The temperature T_{eff} can be written as

$$T_{eff} = T + \tfrac{1}{3} M v_d^2 (1+\beta),\tag{2}$$

where T is the buffer gas temperature and M is the mass of the buffer gas. The collision integral $\Omega^{(1,1)}(T_{eff})$ can be written as

$$\Omega^{(1,1)}(T_{eff}) = \tfrac{1}{2}(k_B T_{eff})^{-3} \int_0^\infty E'^2 Q^{(1)}(E') \exp\left(\frac{E'}{k_B T_{eff}}\right) dE',\tag{3}$$

where the cross section $Q^{(1)}(E')$ is an integral of the classical deflection function $\chi(b, E')$,

$$Q^{(1)}(E') = 2\pi \int_0^\infty \{1 - \cos\chi(b, E')\}\, b\, db;\tag{4}$$

and b is the impact parameter, E' is the centre of mass energy and the deflection function $\chi(b, E')$ is

$$\chi(b, E') = \pi - 2b \int_{r_0}^\infty \left(1 - \frac{b^2}{r^2} - \frac{V(r)}{E'}\right)^{-\frac{1}{2}} \frac{dr}{r^2}.\tag{5}$$

The lower integration limit r_0 in (5) is defined as the outermost root of

$$1 - \frac{b^2}{r_0^2} - \frac{V(r_0)}{E'} = 0.\tag{6}$$

To evaluate equations (3) to (5) we initially calculate the dimensionless reduced collision integrals $\Omega^{(l,s)*}(T^*)$ using a dimensionless interaction potential $V'(r')$. This is related to the actual interaction potential by

$$V'(r') = \frac{1}{\epsilon''} V(r/r_m'').\tag{7}$$

The required collision integrals $\Omega^{(l,s)}(T_{eff})$ are obtained by a second use of the scaling factors ϵ'' and r_m'':

$$\Omega^{(l,s)}(T_{eff}) = \pi r_m''^2 \Omega^{(l,s)*}(T^*),\tag{8}$$

where the reduced temperature T^* is given by

$$T^* = k_B T_{eff}/\epsilon''.\tag{9}$$

The collision integrals are independent of the values of these scale factors. The scale factors have no relationship with the actual well depth ϵ or position of the potential minimum r_m.

The dimensionless parameters α' and β in equations (1) and (2) respectively are negligible at zero field strength. It is also possible to go from mobility data to $V(r)$ (Viehland *et al.* 1976). It has been shown (Gatland *et al.* 1977) that the ion mobility at large E/N is principally determined by $V(r)$ at low r, while the ion mobility at small E/N is determined principally by $V(r)$ at large internuclear separation. It

might therefore be expected that the reduced mobility at zero field strength, $K_0(0)$, would be given by the Langevin model where the potential is just the ion-induced dipole term. This would mean that at zero field strength, the effect of other short range terms is negligible. This is not the case as is demonstrated in this paper.
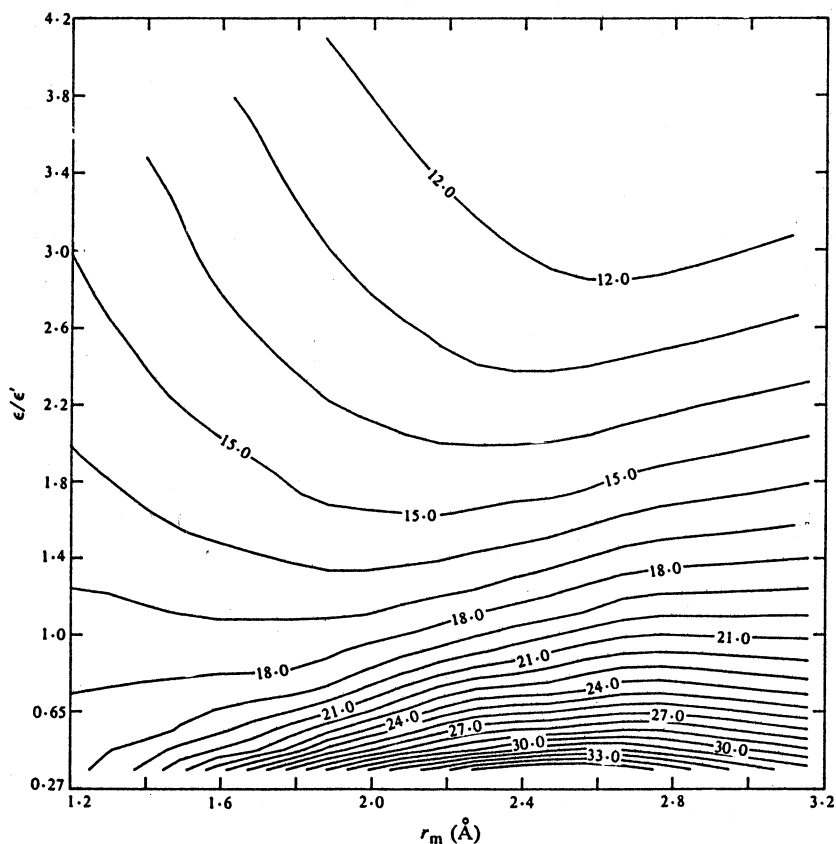

Fig. 1. Contour plot of the zero-field reduced ion mobility $K_0(0)$ over the range $12 \cdot 0$ to $33 \cdot 0 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, shown as a function of the reduced well depth ϵ/ϵ' and the minimum position r_m.

3. Results and Discussion

To explore the effect of the position and depth of the potential energy minimum on the zero-field mobility we used, for a model helium–F^+/F^- interaction potential, an $(n, 6, 4)$ potential of the form

$$V(r) = \frac{n\epsilon}{n(3+\gamma) - 12(1+\gamma)} \left\{ \frac{12}{n}(1+\gamma)\left(\frac{r_m}{r}\right)^n - 4\gamma\left(\frac{r_m}{r}\right)^6 - 3(1-\gamma)\left(\frac{r_m}{r}\right)^4 \right\}, \quad (10)$$

where ϵ and r_m are the depth and position of the potential energy minimum respectively, and the value of the dimensionless parameter γ has been constrained

so that the r^4 term corresponds to the value appropriate to an ion interacting with helium (polarisability is $\alpha = 0 \cdot 204$ Å^3); that is,

$$3\epsilon(1-\gamma)r_m^4 = \alpha q^2/4\pi\epsilon_0 \, ,$$

where ϵ_0 is the vacuum permittivity. In presenting the results of the calculations of zero-field ion mobilities, it was found useful to scale the well depth ϵ by a factor $\epsilon' = \frac{1}{2}\alpha q^2/4\pi\epsilon_0 \, r_m^4$, the value of the ion-induced dipole term at the minimum. In Fig. 1 a contour plot of $K_0(0)$ as a function of ϵ/ϵ' and r_m is presented, obtained using a (12-6-4) potential and a room temperature value of $T = 300$ K. Where the minimum in the potential r_m is at small r, a very large change in ϵ is required to vary $K_0(0)$ by a large amount from the Langevin value for the F$^+$/F$^-$ ion of $16 \cdot 90$ cm^2 V^{-1} s^{-1}. At $r_m = 1 \cdot 2$ Å, $\epsilon' = 0 \cdot 708$ eV (68$\cdot$3 kJ mol^{-1}), but at $3 \cdot 2$ Å, $\epsilon' = 0 \cdot 0140$ eV $= 1 \cdot 35$ kJ mol^{-1}. At large r_m, a very small change in ϵ has a very large effect on $K_0(0)$. For the (12-6-4) potential, at $r_m = 3 \cdot 2$ Å, doubling ϵ from $\epsilon = \epsilon'$ to $\epsilon = 2\epsilon'$, a difference of $0 \cdot 014$ eV to give a slightly more attractive potential, decreases $K_0(0)$ from $21 \cdot 1$ to $15 \cdot 2$ cm^2 V^{-1} s^{-1}. Halving ϵ from $\epsilon = \epsilon'$ to $\epsilon = \epsilon'/2$, to give a slightly more repulsive short range potential, a difference of only $0 \cdot 007$ eV, increases $K_0(0)$ from $21 \cdot 1$ to $27 \cdot 9$ cm^2 V^{-1} s^{-1}. At $r_m = 1 \cdot 2$ Å, the values of $K_0(0)$ at $\epsilon'/2$, ϵ' and $2\epsilon'$ are $18 \cdot 5$, $17 \cdot 5$ and $16 \cdot 0$ cm^2 V^{-1} s^{-1} respectively. If a (8-6-4) potential is used, where the repulsive term is not as steep, essentially the same contour diagram is obtained with the mobilities at small r_m being slightly smaller.

The influence of the ion–atom interaction potential on the macroscopic ion transport properties and the collision dynamics must be taken into account in the estimation of errors in rate coefficients obtained from flow-tube experiments where the diffusion correction is estimated using the Langevin equation.

These observations also have an important consequence when *ab initio* methods are used to calculate $V(r)$. To obtain accurate estimates of $K_0(0)$, the values of $V(r)$ at about 3 Å need to be very accurate [to within better than $0 \cdot 001$ eV to obtain $K_0(0)$ correct to two significant figures]. A basis set that is adequate to describe a bond of length 1–2 Å may not be adequate at a separation of 3 Å. The dependence of the correlation energy on internuclear separation must be correct. These criteria are rarely met in *ab initio* calculations.

References

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