Quantum Phenomena and the Mobility of Potassium Ions in Argon

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Abstract

Recent work on the mobilities of alkali metal ions in the noble gases has indicated that there is a pressure dependence of the zero-field reduced mobility. The possibility of temporarily bound dimers being responsible for this pressure dependence is examined here by quantum mechanical methods for the case of potassium ions in argon and it is shown that the conditions needed for a small pressure dependence do exist at room temperature.

Introduction

In the preceding paper Elford and Milloy (1974, present issue pp. 211–25) have suggested that the cause of an anomalous dependence on gas number density of the mobility of alkali ions in a number of gases is the formation of ion–atom complexes with lifetimes of the order of the mean time between collisions at gas pressures of a few torr. This effect is not included in classical mobility theory based on the Boltzmann equation which assumes that the collisions occur in a time very much less than the mean time between collisions. If this assumption can be shown to be invalid the mobility would be expected to become an explicit function of the gas number density. The purpose of this paper is to examine this assumption by calculating the lifetimes of the ion–atom complexes formed by quantum tunnelling through the centrifugal potential barrier of the system. Although similar calculations have been performed for atom–atom systems (Roberts *et al.* 1969) and the significance of these complexes examined in such phenomena as recombination, there have been only two calculations for ion–atom systems: those of Catlow *et al.* (1970) and Dickinson *et al.* (1972). The system chosen for study was K^+ ions in argon because both a reliable interaction potential is available and the $Ar–K^+$ problem is a severe test of the proposal.

Nature of Ion–Atom Complexes

In the centre of mass frame of reference two colliding particles, if spherically symmetric, move in an effective pair potential

$$\phi_{\text{eff}}(r) = \phi(r) + \hbar^2 l(l+1)/2\mu r^2, \tag{1}$$

where μ is the reduced mass of the colliding pair, l is the angular momentum quantum number and $\phi(r)$ is the potential energy of interaction of the two particles. Two interaction potentials were considered for the $Ar–K^+$ problem, one described by

Kumar and Robson (1973) and the other by Skullerud (1973). Both potentials were of the form given by Mason and Schamp (1958),

$$\phi(r) = \varepsilon\{A(r_m/r)^{12} - B(r_m/r)^6 - C(r_m/r)^4\}, \qquad (2)$$

where ε is the depth of the potential at its minimum position r_m, and had parameters determined by fitting to experimental mobility data as a function of E/N. The Skullerud potential was also fitted to high energy beam data at small distances, the potential being described by an exponential form in this region. However, the calculations reported here do not depend significantly on this region. The coefficients in equation (2) together with the well depths and positions of the zeros in the potentials were as follows.

$\phi(r)$	A	B	C	ε (eV)	r_m (m)
Kumar–Robson	0·61	0·44	1·17	0·114	$3·07 \times 10^{-10}$
Skullerud	0·33333	0·2	1·0	0·137	$2·86 \times 10^{-10}$

Fig. 1a shows the effective pair potential in the Ar–K$^+$ system for four values of l, the potential energy being given by the Kumar–Robson (1973) potential. At low values of l it is possible for particles to be trapped in the negative well of the effective
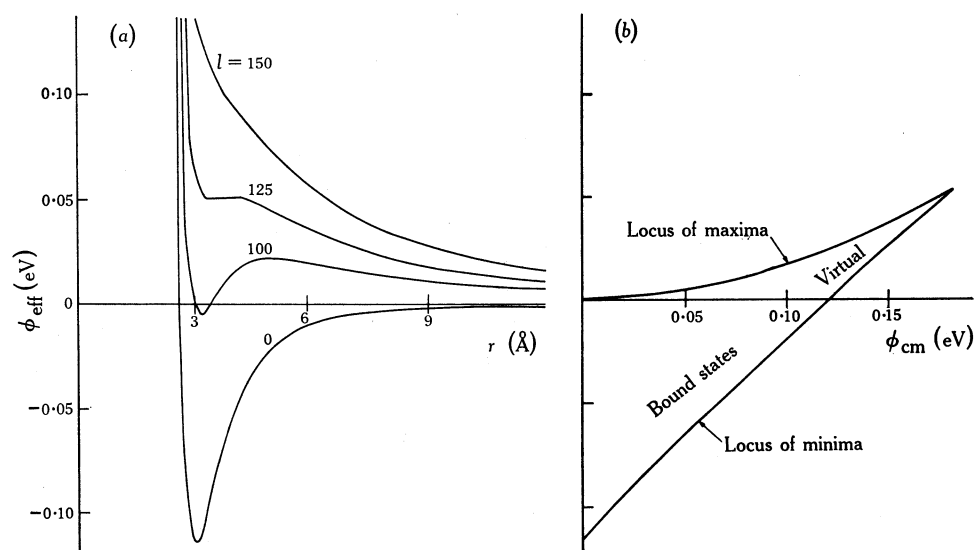

Fig. 1. Effective pair potential $\phi_{eff}(r)$ for the Ar–K$^+$ system using the Kumar–Robson model: (a) form of the potential for four values of the angular momentum quantum number l; (b) loci of the maxima and minima of the potential as a function of the rotational energy ϕ_{cm}.

potential, leading to permanently bound Ar.K$^+$ molecular ions. At intermediate values of l the effective pair potential can support both permanently bound dimers, whose total energy is negative (treating the energy of the separated particles as the zero), and virtual bound states, whose total energy is positive. The virtual states may be dissociated by the process of quantum tunnelling through the rotational barrier, and it is these virtual states that are thought to be responsible for much of the pressure dependence observed in the experimental mobilities. At high values of l there is no

well in the effective pair potential and neither type of bound state can exist. Fig. 1b shows the loci of the minima and maxima in the effective potential as a function of the rotational kinetic energy $\phi_{cm} = \hbar^2 l(l+1)/2\mu r^2$, with the indicated regions in which permanently bound and virtual bound states are found.

The lifetimes of the virtual states depend upon the width of the rotational barrier. States of very low positive energy will have very long lifetimes but will be very difficult to form and poorly populated. On the other hand, states near the top of the barrier will have very short lifetimes but will be heavily populated. If the pressure dependence of the mobility of potassium ions in argon is to be explained by the formation of virtual bound dimers, there must be a number of such states populated at room temperature whose lifetimes are similar to the mean time between collisions. If the lifetimes are very much longer than the mean time between collisions, there will be a very good chance of permanently bound states being formed by deactivating collisions.

Quantum Mechanical Calculations

The low energy elastic scattering of an ion and atom is described by solutions to the radial wave equation

$$-\frac{\hbar^2}{2\mu}(r\psi)'' + \left[\frac{\hbar^2 l(l+1)}{2\mu r^2} + \phi(r) - E\right](r\psi) = 0, \tag{3}$$

where ψ is the radial wavefunction and E is the total energy of the colliding pair. When the interaction potential is zero everywhere the solution to this equation is given by the half-integer Bessel functions and in particular at large distances we have

$$r\psi_l(r) \sim k^{-1}\sin(kr - \tfrac{1}{2}l\pi), \tag{4}$$

where the wave number $k = (2\mu E/\hbar^2)^{\frac{1}{2}}$. For a nonzero interaction potential that is short ranged, as in the current problem, the asymptotic form of the wavefunction is given by

$$r\psi_l(r) \sim k^{-1}\sin(kr + \eta_l - \tfrac{1}{2}l\pi), \tag{5}$$

where η_l is the phase shift. Once the phase shifts have been determined for a number of values of k and l, several properties of the system may be calculated, including the diffusion cross section

$$Q_d(k^2) = 4\pi k^{-2}\sum_{l=0}^{\infty}(l+1)\sin^2(\eta_l - \eta_{l+1}) \tag{6}$$

and hence the first-order (Dalgarno et al. 1958) reduced zero-field mobility

$$\kappa_0 = (e/16\,N_0)(6/k_B T)^{\frac{1}{2}}P^{-1}, \tag{7}$$

where e is the electronic charge, $N_0 = 2\cdot687 \times 10^{19}$ cm^{-3} is the number density of a gas at $273\cdot16$ K and a pressure of 760 torr, T is the temperature and k_B is Boltzmann's constant. The function P is given by

$$P = \tfrac{1}{2}\int_0^{\infty} x^2 Q_d(k^2)\,e^{-x}\,dx, \tag{8}$$

with $x = \hbar^2 k^2/2\mu k_B T$.

The radial wave equation was solved numerically using the standard Numerov method. It was assumed that $r\psi(r)$ was zero for $r < 0.75 R_0$, R_0 being the position of the minimum in the potential energy. After integrating as far as $r = 5R_0$ using a step size of $0.05 R_0$, the step was progressively doubled until it reached a value close to $(2\pi/10k)R_0$, this being about 0.1 of the period of the asymptotic form given by the relation (5). Integration was continued until $r > 10(\varepsilon C/E)^{\frac{1}{3}} R_0 = R_1$, say, as it was found that this gave phase shifts accurate to about four decimal places. After calculating the Bessel functions $J_{l+\frac{1}{2}}(kr)$ and $J_{-l-\frac{1}{2}}(kr)$, the integration was continued for a further 10 steps and the half-integer Bessel functions were recalculated at this new distance, R_2 say. The phase shift was then calculated to an unknown multiple of π using the formula (Kilpatrick *et al.* 1954)

$$\tan\eta_l = (-1)^l \frac{K_1^- - D_1 K_2^-/D_2}{K_1^+ - D_1 K_2^+/D_2}, \qquad (9)$$

where

$$K_i^+ = R_i^{\frac{1}{2}} J_{l+\frac{1}{2}}(kR_i), \quad K_i^- = R_i^{\frac{1}{2}} J_{-l-\frac{1}{2}}(kR_i), \quad D_i = R_i\psi(R_i) \quad (i = 1, 2).$$

To determine the required multiple of π, the number of zeros in $\psi(r)$ between $r = 0$ and R_2 were counted and the number of zeros in the Bessel function $J_{l+\frac{1}{2}}(kr)$ between $r = 0$ and R_2 were obtained using the asymptotic formula for the phase $\theta_v(z)$ of a Bessel function (see Abramowitz and Stegun 1965, p. 365, equation 9.2.29). Given $\theta_{l+\frac{1}{2}}(kR_2)$, the number of zeros before $J_{l+\frac{1}{2}}(kR_2)$ is the integer part $\theta\pi+\frac{1}{2}$. The number of multiples of π to be added to η_l given by equation (9) is the difference between those two totals of zeros. Using this method the phase shifts obtained were accurate to four decimal places and the relative accuracy, required for the lifetime calculations, was greater.

Results

Some of the results from the Kumar–Robson (1973) potential are given in Fig. 2, where the phase shifts in units of π are shown as a function of wave number for seven values of the quantum number l. There are several features of interest in this diagram At very small values of k, each phase shift tends to an integral value and from Levinson's theorem (Mott and Massey 1965) it is known that at $k = 0$ the number of shifts of π in η_l gives the number of permanent bound states supported by the effective pair potential. We see that the pure interaction potential ($l = 0$) supports 39 bound states if it is represented by the Kumar–Robson model; this number is also given by the Skullerud (1973) potential. From Fig. 1a we see that bound rotational states are allowed up to $l \sim 100$, and for the Kumar–Robson potential 1845 bound states were identified with values of $l \leqslant 101$. The Skullerud potential, which is deeper than the Kumar–Robson form, supports bound states at larger values of l. No attempt has been made to calculate the energies of these bound states.

Phase shifts calculated for values of $l > 5$ begin to show sharp increases at certain values of k. When these increases are equal to π they are identified with the virtual states thought to be responsible for the small pressure dependence in the potassium ion mobilities. The energy of the virtual state is given by $E_i = \hbar^2 k_i/2\mu$, where k_i is the value of k at which the phase shift is changing most rapidly with k, and the lifetime τ_i
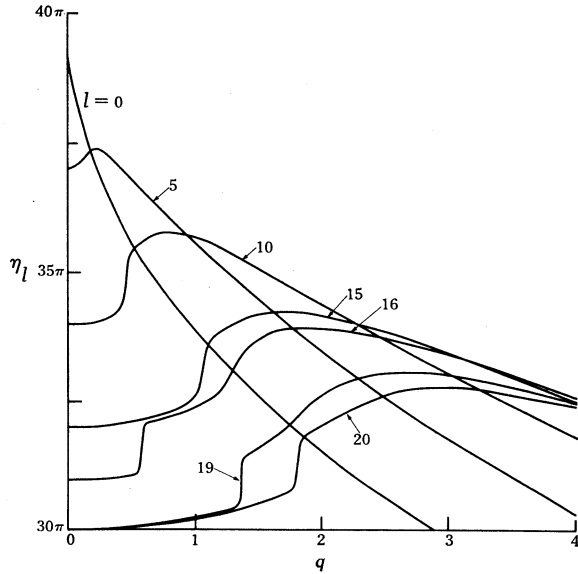
Fig. 2. Phase shifts η_l in units of π as a function of the dimensionless parameter $q = kR_0$ from the Kumar–Robson potential for the indicated values of the angular momentum quantum number l.
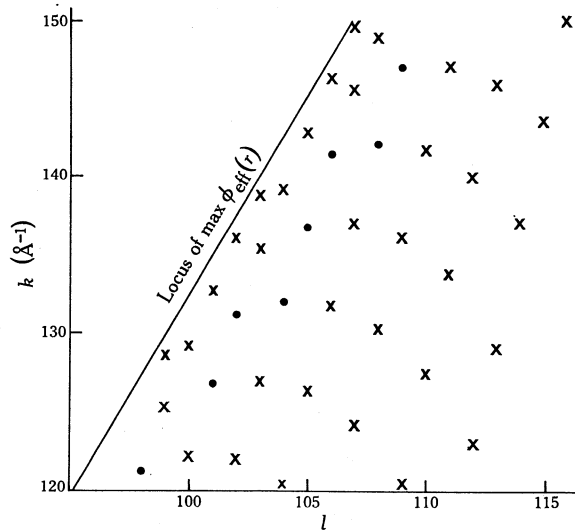

Fig. 3. Wave numbers k as a function of the angular momentum quantum number l for virtual states from the Skullerud potential with centre of mass energies approximately in the range 20–30 meV. The solid circles indicate the states that are probably responsible for the observed pressure dependences.

of that state is obtained from the maximum slope,

$$\tau_i = \tfrac{1}{2}\hbar(\partial\eta_l/\partial E)_{\max}. \tag{10}$$

It is possible for a given rotational state to support several virtual states, and more than 450 virtual states were identified for both potential models. These states had energies up to 60 meV and lifetimes greater than 10^{-13} s, many of them with lifetimes greater than 10^{-7} s. Thus, at least in principle, it is possible for virtual states to influence mobility measurements.

Table 1. **Energies and lifetimes of virtual states lying between approximately 20 and 30 meV**

Asterisks indicate those states that could contribute substantially to the pressure dependence

l	E (meV)	τ (ns)	E (meV)	τ (ns)	E (meV)	τ (ns)	E (meV)	τ (ns)
98	19·70	0·1591*						
99	21·03	0·0087	22·14	0·0003				
100	19·99	>32	22·35	0·0025				
101	21·54	22·4564*	23·61	0·0008				
102	19·90	>33	23·06	0·2076*	24·80	0·0005		
103	21·64	>32	24·58	0·0058	25·80	0·0003		
104	19·43	>34	23·37	29·1554*	25·99	0·0027		
105	21·34	>32	25·08	5·9749*	27·38	0·0008		
106	23·25	>31	26·81	0·168*	28·66	0·0005		
107	20·63	>33	25·17	>30	28·40	0·0218	29·97	0·0003
108	22·72	>32	27·05	28·0483*	29·98	0·0034		
109	19·47	>34	24·81	>30	28·93	0·2062*		
110	21·73	>32	26·90	>29				
111	24·00	>31	28·99	>28				
112	20·25	>33	26·28	>29				
113	22·71	>31	28·56	>28				
114	25·17	>30						
115	27·64	>29						
116	30·10	>27						

Fig. 3 shows some of the wave numbers at which virtual states are found using the Skullerud (1973) potential for centre of mass energies lying between about 20 and 30 meV, the energies most likely to be significant at room temperature. It is obvious from the figure that the wave numbers of the states lie on smooth curves and that for a given value of l the states are closer together at higher k. Table 1 gives the energies and lifetimes of the states represented in Fig. 3. The lifetimes range from about 3×10^{-13} s to those in excess of 3×10^{-8} s and the states with the higher energies have the shorter lifetimes, as is to be expected since the rotational barrier is narrower at higher energies. The states lying close to the limiting curve of dissociation have very short lifetimes and it was sometimes difficult to distinguish these states from perturbations in the phase shift that occurred at energies a little higher than the maximum in the effective potential. At room temperature and at the pressures of 1 or 2 torr used by Elford and Milloy (1974) in their experiments, the mean time between collisions is of the order of 1 ns. From Table 1 it is seen that there are eight states (asterisks) whose energies and lifetimes are such that they could contribute significantly to the pressure dependence. These states are indicated in Fig. 3 (by solid circles) and we see that they all have

either the second highest or highest energy for a given rotational quantum number. Although there are many states whose lifetimes are much longer than those selected, they are all buried deeply in the well behind the rotational barrier and it is unlikely that their populations are very high. Similar results to the above were obtained for the Kumar–Robson (1973) potential.
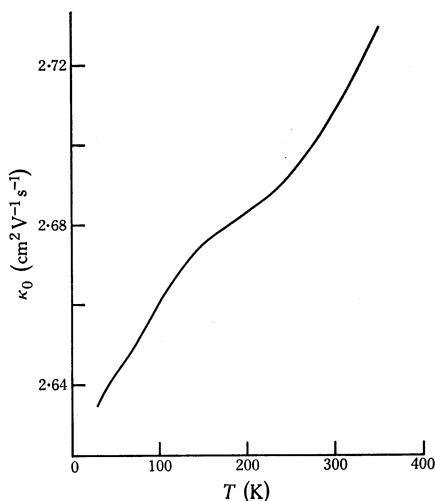

Fig. 4. Variation with temperature of the first-order reduced zero-field mobility κ_0 of potassium ions in argon, as calculated from equations (6)–(8).

It is possible that quantum effects due to the virtual bound states could be seen in the temperature dependence of the reduced zero-field mobilities. Fig. 4 shows the first-order reduced zero-field mobility for the system as a function of temperature, calculated using equations (6)–(8). The results do not indicate any marked quantum effects and the variations shown are only slightly greater than the claimed errors in experiment. Consequently it is unlikely that any temperature-dependent quantum effects could be observed experimentally. However, the pressure dependence due to the formation of virtual bound states is not excluded by these mobility calculations.

Conclusions

In this investigation of the possibility of quantum effects being responsible for small pressure dependences in potassium ion mobility data, it has been shown, using two realistic ion–atom interaction potentials, that a number of virtual bound states with lifetimes typical of the mean time between collisions will be populated at ambient temperatures and that, in addition, a large number of permanently bound states could be formed in principle. The question of the ease of formation of such states can only be answered by carrying out multichannel scattering calculations, which is beyond the scope of the present work. As the Ar–K$^+$ system is not expected to show quantum effects easily, due to the large masses involved, it can be expected that other alkali metal ion – inert gas systems will also form virtual and permanently bound dimers.

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