AD-A142 334   THE TRANSFER OF ATOMS IONS AND MOLECULAR GROUPS IN SOLUTION PART 2 TUNNEL..(U) OAKLAND UNIV ROCHESTER MICH DEPT OF CHEMISTRY P P SCHMIDT 30 OCT 83 13   1/1

UNCLASSIFIED   N00014-77-C-0293   F/G 20/12   NL

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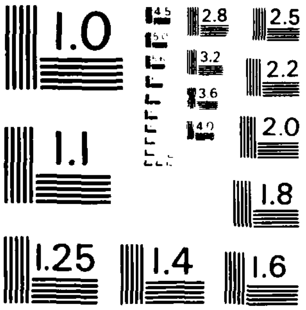

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OFFICE OF NAVAL RESEARCH

Contract No. N00017-77-C-0239

Task No. NR 359-648

The transfer of atoms, ions and molecular groups in solution. Part 2.--Tunnelling between harmonic wells

by

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Prepared for Publication in the

Oakland University
Department of Chemistry
Rochester, Michigan 48063

October 1983

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER 13

2. GOVT ACCESSION NO. AD-A142 334

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle) The transfer of atoms, ions and molecular groups in solution. Part 2.--Tunnelling between harmonic wells

5. TYPE OF REPORT & PERIOD COVERED ~~5/1/83 to 4/31/~~84

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s) P. P. Schmidt

8. CONTRACT OR GRANT NUMBER(s) N00014-77-C-0239

9. PERFORMING ORGANIZATION NAME AND ADDRESS

Department of Chemistry
Oakland University
Rochester, Michigan 48063

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 359-648

11. CONTROLLING OFFICE NAME AND ADDRESS

kr. Jerry Smith, Code 472, Office of Naval Research, Arlington, VA 22217

12. REPORT DATE October 30, 1983

13. NUMBER OF PAGES 10

14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)

15. SECURITY CLASS. (of this report)

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for Public Release
Distribution Unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

To appear: J. Chem. Soc. Faraday 2, 1984

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Atom transfer, reactions, solution

is considered

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

~~We consider~~ The use of a harmonic-oscillator model to investigate the tunnelling of atoms, ions and molecular groups between positions of equilibrium for systems in condensed phases. The use of the oscillator model is warranted in many instances for which one has reasonably accurate information about the vibrational frequencies of atoms or molecular groups together with information about the distance over which the species transfers.

Thus, the harmonic-oscillator model can be used in the absence of more complete information to make extimates of the rates of various kinds of heavy-centre transfers in solution. In this paper we present a general treatment for the determination of the tunnel factors which are involved in the transfer. The work constitutes an extension of the analysis of Wall and Glockler who used a symmetric double potential well in order to investigate the resonance doubling of the vibrational spectrum of ammonia. We consider the general problem of the tunnelling between any two vibrational states of the separate potential wells. As an example we apply the analysis to the consideration of a simple ion transfer between two centres of solvation

A1

The Transfer of Atoms, Ions and Molecular Groups in Solution. II. Tunnelling between harmonic wells

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Abstract

We consider the use of a harmonic oscillator model to investigate the tunnelling of atoms, ions, and molecular groups between positions of equilibrium for systems in condensed phases. The use of the oscillator model is warranted in many instances for which one has reasonably accurate information about the vibrational frequencies of atoms or molecular groups together with information about the distance over which the species transfers. Thus, the harmonic oscillator model can be used in the absence of more complete information to make estimates of the rates of various kinds of heavy-centre transfers in solution. In this paper we present a general treatment for the determination of the tunnel-factors which are involved in the transfer. The work constitutes an extention of the analysis of Wall and Glockler who used a symmetric double potential well in order to investigate the resonance doubling of the vibrational spectrum of ammonia. We consider the general problem of the tunnelling between any two vibrational states of the separate potential wells. As an example, we apply the analysis to the consideration of a simple ion-transfer between two centres of solvation.

Introduction

The transfer of an atom, ion or molecular group from one location to another in a condensed phase was considered in Part I.[1] There, methods were developed which make use of accurate pair-wise potential energy functions to determine the magnitudes of the matrix elements which govern the transfer. For solution chemistry it is clear that it may not generally be possible to use accurate potential energy functions, as few accurate functions have been determined. Thus, it is difficult to construct rate constants and to establish links between structural and kinetic factors of the kind considered[1] without corroborating experimental data of different kinds.

In this paper we consider the use of the relatively simple double harmonic potential well in order to describe the parametric interaction between a transferrable species at one location and its eventual location at a physically removed side. We show that it is possible to make an estimate of the size of the matrix elements which couple the initial and final states of the system. These estimates can be made with only the frequencies of vibration of the transfer-species in its initial and final states and the distance over which the species tunnels. As the analysis of Wall and Glockler[2] on the inversion tunnelling of ammonia showed, the height of the energy barrier between the initial and final states can be as much as 50% in excess of the true value. Yet, with the use of simple perturbation theory, Wall and Glockler's analysis is surprisingly accurate. The height of the barrier for the ammonia inversion has been accurately estimated by Swalen and Ibers.[3]

In this paper the Wall-Glockler analysis[2] is extended and applied to the general, asymmetric, harmonic double potential well. The results of the generalization are applied to the determination of the rate constant for the tunnelling of a heavy-centre from one location to another. We present a general analysis which parallels that of Part I. The specific difference between this work and that of Part I is the use of the double potential well instead of considering the specific pair-wise potential energy functions which operate between the transfer-species and its surrounding solvent or ligand.

In the next section, we summarize the Born-Oppenheimer-Holstein[4] separation which was developed in Part I Following that summary, we present specific forms for the matrix elements which arise from the consideration of the double potential well. Finally, the results are applied to a model type of ion transfer.

Born-Oppenheimer-Holstein Analysis: Summary

The Hamiltonian operator for the entire reactive system is expressed as

$$H = H_t + H_{env} \tag{1}$$

in which H_t is that part of the total operator which applies to the transfer-species and H_{env} is the remainder. The operator H_t is expressed further as

$$H_t = T + V \tag{2}$$

in which T is the momentum operator and V is the potential. These operators usually can be specified in one dimension for the motion of the transfer-species along the *transfer-axis*.[1]

The complete eigenvalue problem is written as

$$H\Psi = E\Psi \tag{3}$$

with

$$\Psi = \sum_{i,\gamma} X_{i\gamma} \phi_{i\gamma} \tag{4}$$

in which the basis functions $\phi_{i\gamma}$ are harmonic oscillator functions which are referred to coordinate origins at the locations i (i = a or b, the labels for the initial and final locations of the transfer-species). The elements $X_{i\gamma}$ of the vector $\underset{\sim}{X}$ are in essence the vibrational wavefunctions for the environment. A particular element of the vector $\underset{\sim}{X}$ is determined by the equation

$$H_{i\gamma,i\gamma} X_{i\gamma} = \sum_{j,\delta}{}' L_{i\gamma,j\delta} X_{j\delta} \tag{5}$$

in which the L-matrix elements are defined by

$$L_{i\gamma,j\delta} = \sum_{k,\epsilon} S^{-1}_{i\gamma,k\epsilon} V^j_{k\epsilon,j\delta} \tag{6}$$

The $S^{-1}_{i\gamma,k\epsilon}$ are elements of the inverse of the overlap matrix The diagonal matrix element $H_{i\gamma,i\gamma}$ is given by

$$H_{i\gamma,i\gamma} = E - E^0_{i\gamma} - L_{i\gamma,i\gamma} - T \tag{7}$$

in which $E^0_{i\gamma}$ is the eigenvalue of the harmonic oscillator Hamiltonian operator for the transfer-species at the location i. Finally, the potential energy operator V^j, which enters the matrix elements $V^j_{k\epsilon,j\delta}$ in eqn (6), is defined as

$$V^j = V - \tfrac{1}{2}kz_j^2 \tag{8}$$

for which z is defined to be the transfer-axis, and k_j is the harmonic oscillator force constant which is defined with reference to the coordinates at the origin j. This form for the potential is used in order to isolate the local harmonic oscillator Hamiltonian operators.[1]

In the next section, the matrix elements $V^j_{k\epsilon,j\delta}$ which contribute to the $L_{i\gamma,j\delta}$, eqn (6), are determined for the general asymmetric double harmonic potential well.

Matrix Elements: evaluation

The general form of the asymmetric double potential well is illustrated in Figure 1. The actual potential is specified as

$$V(z) = \tfrac{1}{2}k_a z_a^2 - V_0 \qquad -\infty \le z \le 0$$

$$= \tfrac{1}{2}k_b z_b^2 \qquad 0 \le z \le \infty \tag{9}$$

in which $-V_0$ is a constant displacement in energy of the left hand well relative to the right. In terms of a Taylor series expansion, $-V_0$ represents the difference $V_b(z_b^0) - V_a(z_a^0)$, the difference between the separate zeroth order terms of the expansion; note, V_0 can be negative, in which case the right hand well is lower in energy than the left.

The intersection of the two wells is defined to be the origin of the system of coordinates. The distances from the origin to the minima of the two wells are ℓ_a (to the left) and ℓ_b (to the right). If ℓ_b is known, for example, then

$$\ell_a = \{(k_b/k_a)\ell_b{}^2 + 2V_0/k_a\}^{\frac{1}{2}}. \tag{10}$$

With $R = \ell_a + \ell_b$, one finds

$$\ell_a = \frac{R}{1-k_a/k_b}\left[1 \pm \left\{k_b/k_a + 2(1 - k_b/k_a)V_0/k_aR\right\}^{\frac{1}{2}}\right]. \tag{11}$$

However, if $k_a = k_b$, then

$$\ell_a = \tfrac{1}{2}R + V_0/kR. \tag{12}$$

For the evaluation of the integrals, the distances ℓ_a, ℓ_b and R are specified individually. The relationships between these quantities are as given in eqn (10) to (12).

The modified potential energy operator V^j ($j=a,b$), eqn (8),

is used in

$$\begin{aligned}V^b_{am,bn} &= \langle am|V^b|bn\rangle \\ &= \int_{-\infty}^{0} dz\{\tfrac{1}{2}k_a z_a^2 - V_0\}\phi_m(z_a)\phi_n(z_b) \\ &+ \tfrac{1}{2}k_b\int_0^{\infty} dz\ z_b^2\phi_m(z_a)\phi_n(z_b) - \tfrac{1}{2}k_b\int_{-\infty}^{\infty} dz\ z_b^2\phi_m(z_a)\phi_n(z_b) \\ &= \tfrac{1}{2}\int_{-\infty}^{0} dz\{k_a z_a^2 - k_b z_b^2 - 2V_0\}\phi_m(z_a)\phi_n(z_b)\end{aligned} \tag{13}$$

The specific form is used here for the simple reason that there are only two centres, a and b, and the exchange of indices converts one to the other.

The integrals in eqn (13) are evaluated with the use of the one-dimensional harmonic oscillator basis functions:

$$\phi_n(z) = (a/2^n\pi n!)^{\frac{1}{2}}H_n(az)\exp(-\tfrac{1}{2}a^2z^2) \tag{14}$$

in which $H_n(az)$ is the Hermite polynomial. In the treatment of the general form of matrix element, it is necessary to refer the product of the wavefunctions to a single centre. This is accomplished as follows. The exponential part combines as

$$\exp\{-\tfrac{1}{2}(a^2z_a^2 + b^2z_b^2)\} = \exp\left(-\tfrac{1}{2}(a^2+b^2)y^2 - \frac{a^2b^2}{2(a^2+b^2)}R^2\right) \tag{15}$$

with y defined as

$$y = z + d, \tag{16}$$

and

$$d = \frac{a^2 R_a - b^2 R_b}{a^2 + b^2} \tag{17}$$

For the single-centre matrix element, R = 0, and eqn (15) reduces to $\exp(-a^2 z^2)$

The matrix element, eqn (13), can be written as

$$\langle am|V^b|bn\rangle = \tfrac{1}{2}\left[\frac{a^2+b^2}{2^{m+n+1}\pi m!n!}\right]^{\frac{1}{2}} S_{00}(-1)^{m+n}\int_{-d}^{\infty} dy\left[(k_a - k_b)y^2\right.$$

$$\left. - 2(k_aR_b + k_bR_a)y + k_aR_b^2 - k_bR_a^2 - 2V_0\right]$$

$$\times H_m\left(a(y-R_b)\right)H_n\left(b(y+R_a)\right)\exp\left(-\tfrac{1}{2}(a^2+b^2)y^2\right) \tag{18}$$

in which S_{00} is the ground state overlap:

$$S_{00} = \left(\frac{a^2b^2}{a^2+b^2}\right)^{\frac{1}{2}}\exp\left(-\frac{a^2b^2}{2(a^2+b^2)}R^2\right) \tag{19}$$

and

$$R_a = \frac{a^2}{a^2+b^2}R$$

$$R_b = \frac{b^2}{a^2+b^2}R. \tag{20}$$

It is apparent that the general integral

$$\int_{-d}^{\infty} dy\; y^p H_m\left(a(y-R_b)\right)H_n\left(b(y+R_a)\right)\exp\left(-\tfrac{1}{2}(a^2+b^2)y^2\right) \tag{21}$$

with p = 0,1,2, must be evaluated. The addition theorem for the Hermite polynomials is[5]

$$H_m[a(y\pm R)] = \frac{1}{2^{m/2}}\sum_{k=0}^{m}\binom{m}{k}(\pm 1)^{m-k}H_{m-k}(\sqrt{2}aR)H_k(\sqrt{2}y) \tag{22}$$

where $\binom{m}{k}$ is the binomial coefficient. Further, the general form of the Hermite polynomial is[6]

$$H_m(x) = \sum_{s=0}^{[m/2]}(-1)^s(2x)^{m-2s}\,\frac{m!}{(m-2s)!s!}\;; \tag{23}$$

the notation [m/2] indicates that the integer of m/2 is to be taken.

With the use of the expansions, the matrix element can be expressed as

$$\langle am|V^b|bn\rangle = \frac{1}{2^{m+n+2}}(\pi m!n!)^{-\frac{1}{2}}S_{00}\sum_{k=0}^{m}\sum_{\ell=0}^{n}\binom{m}{k}\binom{n}{\ell}(-1)^{n-k}$$

$$\times H_{m-k}(\sqrt{2}aR_b)H_{n-\ell}(\sqrt{2}bR_a)2^{2(k+\ell)}\left(\frac{a^2b^2}{a^2+b^2}\right)^{\frac{1}{2}(k+\ell)}k!\ell!$$

$$\times\sum_{s=0}^{[k/2]}\sum_{t=0}^{[\ell/2]}\frac{(-1)^{s+t}}{(k-2s)!(\ell-2t)!s!t!}\left(\frac{a^2+b^2}{4\sqrt{2}a^2b^2}\right)^{s+t}\left[(k_a - k_b)\right.$$

$$\times\left(\frac{2}{a^2+b^2}\right)\Gamma\left(\frac{k+\ell+3}{2}-s-t,D^2\right) - 2(k_aR_b + k_bR_a)\left(\frac{2}{a^2+b^2}\right)^{\frac{1}{2}}$$

$$\left.\times\Gamma\left(\frac{k+\ell+2}{2}-s-t,D^2\right) + (k_aR_b^2 - k_bR_a^2 - 2V_0)\Gamma\left(\frac{k+\ell+1}{2}-s-t,D^2\right)\right] \tag{24}$$

where $D^2 = \frac{1}{2}(a^2+b^2)d^2$ and the incomplete gamma function is[5]

$$\Gamma(a,x) = \int_x^{\infty} dt\; t^{a-1}e^{-t} \tag{25}$$

The single-centre matrix element can be obtained in principle from the two-centre form, but it is actually simpler to consider the specific form:

$$\langle am|V^a|an\rangle = \tfrac{1}{2}\,\frac{a}{(2^{m+n}\,m!n!\,)^{\frac{1}{2}}}\int_{-\infty}^{0} dz\ (k_a z_a^2 - k_b z_b^2 - 2V_0)H_m(az_a)$$

$$\times H_n(az_a)\exp(-a^2 z_a^2). \tag{26}$$

The same type of analysis, as applied to the two-centre form, yields

$$\langle am|V^a|an\rangle = \tfrac{1}{4}\hbar\omega_a\left(\frac{2^{m+n}}{\pi m!n!}\right)^{\frac{1}{2}} \sum_{s=0}^{[m/2]}\ \sum_{t=0}^{[n/2]}(-1)^{s+t}\ 4^{-s-t}$$

$$\times\frac{m!n!}{(m-2s)!(n-2t)!s!t!}\left\{(1 - k_b/k_a)\Gamma\left(\frac{m+n+3}{2} -s-t,q_a^2\right)\right.$$

$$- 2(k_b/k_a)aR\Gamma\left(\frac{m+n+2}{2} -s-t,q_a^2\right) - \left((k_b/k_a)(aR)^2\right.$$

$$\left.\left. + 2V_0/\hbar\omega_a\right)\Gamma\left(\frac{m+n+1}{2} -s-t,q_a^2\right)\right\} \tag{27}$$

for which q_a is

$$q_a = at_a.$$

q_b is defined similarly.

Finally, the general overlap integral is written as

$$S_{mn} = \sum_{k=0}^{m}\ \sum_{\ell=0}^{n}\binom{m}{k}\binom{n}{\ell}\ \frac{(-1)^{m-k}}{2^{(m+n)/2}}\, H_{m-k}(\sqrt{2}aR_b)H_{n-\ell}(\sqrt{2}bR_a)$$

$$\sum_{s=0}^{[k/2]}\ \sum_{t=0}^{[\ell/2]}\frac{k!\ell!}{(k-2s)!(\ell-2t)!s!t!}(-1)^{s+t}(2\sqrt{2})^{k+\ell-2(s+t)}$$

$$\times a^{k-2s}b^{\ell-2t}\,\frac{(k+\ell-2(s+t)-1)!!}{2(a^2+b^2)^{(k+\ell+1)/2-s-t}} \tag{28}$$

and

$$k+\ell-2(s+t) = \text{even}.$$

Model System Calculation. Asymmetric ground-to-ground state transfer

The simplest direct application of the methods which have been developed above is to the consideration of the ground-to-ground state transfer of a heavy-centre from one harmonic well to another. The wells need not be symmetric with respect to their widths nor with respect to their relative locations on the energy-axis. According to the transition state theory, the convolution of environmental energies ensures the conservation of total energy for the transfer; the energy deficit for the reactive subsystem is made up from contributions from the environment.

In this section attention focuses entirely upon the problem of determining the size of the matrix elements $L_{a0,b0}$ in the diabatic limit. For the ground state transfer, we need specifically to consider the element

$$L_{a0,b0} = (V^b_{a0,b0} - S_{00}V^b_{b0,b0})/(1 - S_{00}^2). \tag{29}$$

The matrix element $V^b_{a0,b0}$ is

$$V^b_{a0,b0} = \langle a0|V^b|b0\rangle$$

$$= \tfrac{1}{2}\hbar\omega_b S_{00}\left\{\frac{1}{2\sqrt{\pi}}\left[\frac{2}{1+a^2/b^2}(1 + k_a/k_b)\Gamma(3/2,D^2)\right.\right.$$

$$- 2\left(\frac{2}{1+a^2/b^2}\right)^{\frac{1}{2}} b\left((k_a/k_b)R_b + R_a\right)\Gamma(1,D^2) + \left((bR_a)^2\right.$$

$$\left.\left. + (k_a/k_b)(bR_b)^2 - 2V_0/\hbar\omega_b\right)\Gamma(\tfrac{1}{2},D^2)\right]$$

$$\left. - \frac{1}{1+a^2/b^2}\left[1 + \frac{(bR)^2}{1+a^2/b^2}\right]\right\} . \tag{30}$$

The matrix element $V^b_{b0,b0}$ is

$$V^b_{b0,b0} = \langle b0|V^b|b0\rangle$$

$$= \frac{1}{4\sqrt{\pi}}\hbar\omega_b\left\{(k_a/k_b - 1)\Gamma(3/2,q_b^2) - 2(k_a/k_b)bR\Gamma(1,q_b^2)\right.$$

$$\left. + \left[(k_a/k_b)(bR)^2 - 2V_0/\hbar\omega_b\right]\Gamma(\tfrac{1}{2},q_b^2)\right\} . \tag{31}$$

The vibrational overlap element for the ground states is given by eqn (19).

The general formulae for the matrix elements can be simplified in many instances with the use of various limiting forms. The limits generally involve the consideration of large or small values of the arguments of the incomplete gamma functions. The typical values of ϵ_a, ϵ_b, and the several R's, together with the coefficients a and b, lead to terms, *e.g.*, q_a, D, *etc.*, which are large or small in a limiting sense.

For integer n, the incomplete gamma function $\Gamma(n,x^2)$ is[5,6]

$$\Gamma(n,x^2) = (n-1)!\,e^{-x^2}\sum_{s=0}^{n-1} x^{2s}/s! \tag{32}$$

while for half-integer arguments, $n+\frac{1}{2}$, one has[5,6]

$$\Gamma(n+\tfrac{1}{2},x^2) = \frac{(2n-1)!!}{2^n}\left[\sqrt{\pi}\,\mathrm{erfc}(x) + e^{-x^2}\sum_{s=0}^{n-1}\frac{2^{s+1}x^{2s+1}}{(2s+1)!!}\right] \tag{33}$$

in which erfc(x) is the complement of the error integral:

$$\mathrm{erfc}(x) = \frac{2}{\sqrt{\pi}}\int_x^{\infty} dt\, e^{-t}$$

$$= 1 - \mathrm{erf}(x). \tag{34}$$

In the limit as x vanishes,

$$\lim_{x\to 0}\Gamma(a,x^2) = \Gamma(a). \tag{35}$$

Conversely, as x becomes large ($x > 3$), $\mathrm{erfc}(x) \doteq 0$, and

$$\lim_{x>3}\Gamma(n+\tfrac{1}{2},x^2) = \frac{(2n-1)!!}{2^n}\,e^{-x^2}\sum_{s=0}^{n-1}\frac{2^{s+1}x^{2x+1}}{(2s+1)!!}. \tag{36}$$

The application of these limiting forms to the matrix elements results in a considerable simplification. In order to apply these limiting forms, however, it is necessary to consider the physical distinctions within the system which will govern the types of limits which one may expect to use.

A number of possible limits can be considered, these limits are specified through the consideration of differences in the reduced masses in the initial and final states, differences in the lengths ℓ_a and ℓ_b, and differences in the force constants. For the consideration of the transfer of a simple solvated ionic species (for example, a sodium cation) from one cage of solvent to another in a homogeneous, single solvent system, it is clear that (effectively) all quantities in the final state are the same as in the initial state. The double harmonic well representation is symmetric. *Thus, clearly, the quantity $D = 0$.* On the other hand, it is possible to use the harmonic oscillator representation developed here to consider the matrix element for the transfer of a simple cation (again, sodium) from one solvent system to another. In this case, as we now show, we can still obtain a relatively simple limiting form for D and the other quantities.

We consider the hypothetical transfer of a simple cation across the interface of two polar, but immiscible liquids, for example, across the water-propylene carbonate interface. Although in any interface there do not occur discontinuous changes in composition, there may be sufficiently different structures of solvation at some point to ensure that the ion-transfer between these structures is rate-determining. We model such a situation.

The purpose in using the harmonic oscillator well model, as stated, is to be able to make reasonable estimates of the transfer matrix elements with the use of available data. The data which are needed in order to consider the interfacial ion-transfer are simply the fundamental frequencies for the oscillation of the ion in its initial and final cages of solvent and the distance

over which the transfer takes place.

Studies of the far-infrared spectra of solvated cations of Group I, [illegible], sodium, [illegible], indicate a relatively small solvent-dependence,[7] that is, the change from one solvent to another results in a shift of the spectral maximum [illegible] relatively small amount. The changes in the reduced mass [illegible]ssing from one solvent to another are small as well. Th[illegible] would appear to be *reasonable*, as a first approximation, to [illegible]e the differences in mass in considering the transfer matr[illegible]s. Moreover, *if one can ignore the differences in mass,* [illegible], as observed,[7] the spectra in several solvents are essentially the same, then it is also reasonable to assume that the force constants are effectively similar for the initial and final states of the ion-transfer. With the use of these two (apparently extreme) assumptions, it is easy to show that D reduces to

$$D \doteq V_0/2\hbar\omega aR \tag{37}$$

in which ω is now the common frequency and R is still the total distance for the transfer. V_0 characterizes the relative displacement of one potential energy function (from which the second derivative yields the force constant) with respect to another. Thus, this quantity must necessarily reflect the total interaction of the ion with its surroundings. As such, V_0 is effectively the change in free energy for the ion in one cage of solvent compared to the other.

If we assume, for sodium, that $\omega \sim 200\ \text{cm}^{-1}$, and $R \sim 0.6\ \text{Å}$, we find

$$D \simeq 2\delta V \quad (V \text{ in eV}) \qquad (38)$$

It is apparent that large differences in the free energy of solvation will result in one limiting form (through the $V^b_{a0,b0}$ matrix element) and a vanishing difference in the free energy leads to the opposite limiting form.

It is also clear that any real system, even if modelled minimally with the use of this double harmonic well potential, must exhibit a complicated collection of changes in all of the quantities which we have considered. Thus, in fact, it should not generally be possible to reduce most transfers to the limit expressed in eqn (37). Nevertheless, this limit is useful for graphically showing how the quantity D can assume values which yield different limiting forms for the incomplete gamma functions.

In general, the q-quantities satisfy the large-argument limit for the incomplete gamma functions. We conclude this section by considering the two extreme limits D → 0 and D > 3 for the $L_{a0,b0}$ matrix element as expressed by eqn (29)-(31).

First, the large q-limit for the matrix element $\langle b0|V^b|b0\rangle$ is

$$\lim_{q>3}\langle b0|V^b|b0\rangle = \frac{1}{4\sqrt{\pi}}\hbar\omega_b\left\{q - (k_a/k_b)(q+2bR)\right\}e^{-q^2}. \qquad (39)$$

In the limit of a symmetric well system, this simplifies further; $k_a/k_b = 1$. The large D-limit for the two-centre matrix element is given by

$$\lim_{D>3}\langle a0|V^b|b0\rangle = -\tfrac{1}{2}\hbar\omega_b S_{00}\left\{\frac{1}{2\sqrt{\pi}}\left[\frac{2D}{1+a^2/b^2}(1+k_a/k_b)\right.\right.$$
$$+ 2\left(\frac{2}{1+a^2/b^2}\right)^{\frac{1}{2}} b\left((k_a/k_b)R_b + R_a\right)\Bigg]e^{-D^2}$$
$$\left. + \frac{1}{1+a^2/b^2}\left(1 + \frac{(bR)^2}{1+a^2/b^2}\right)\right\}. \qquad (40)$$

In contrast, the small D-limit is given by

$$\lim_{D\to 0}\langle a0|V^b|b0\rangle = \tfrac{1}{2}\hbar\omega_b S_{00}\left\{(k_a/k_b - 1)\frac{1}{1+a^2/b^2}\right.$$
$$- 2\left((k_a/k_b)\xi_a + \xi_b\right)b\left(\frac{2}{1+a^2/b^2}\right)^{\frac{1}{2}} + \left((k_a/k_b)\xi_a^2\right.$$
$$\left. - \xi_b^2\right)b^2 - 2V_0/\hbar\omega_b\Bigg\} \qquad (41)$$

For an essentially symmetric well, this reduces to

$$-\hbar\omega_b S_{00}\eta.$$

It is worth noting in eqn (40) the fact that although an apparent direct dependence on V_0 disappears in the limiting process, nevertheless, V_0 still plays a role in the matrix element through the quantity D.

Turning our attention to the tunnelling of a small cation, such as lithium, from one cage of solvent to another in solution, we find the following. First, assume that the system satisfies the limits for a symmetric well model, that is, the initial and final states are physically the same. In this case, it is easy to find

$$L_{a0,b0} = -\frac{1}{\sqrt{2}}\hbar\omega q\, e^{-q^2} \qquad (42)$$

If, for lithium, we assume that $\omega \approx 430\ \mathrm{cm}^{-1}$ (which is a reasonable value based on the far infrared spectrum of lithium in a number of solvents[7]) and $r \approx 0.3$ Å, then $L_{a0,b0} \approx 0.05\ \mathrm{kJ\ mol}^{-1}$. As pointed out in Part I[1], this value satisfies the diabatic limit for the transfer. It remains to be demonstrated whether a value for the transfer matrix element $L_{a0,b0}$ which is obtained in this fashion is an accurate estimate. It is clear that it is a reasonable and consistent value when it is compared with the values which were generated in Part I by means of the use of more complete and accurate potential energy functions.

Discussion and Summary

The effects of the environment on the matrix elements have not been specifically included here, as they were in Part I.[1] The reason is simple. As was argued in Part I, the specific consideration of the environmental contributions to the matrix elements for the transfer could be reduced to additional terms which are of the same general form as V^j which is defined for the reactive subsystem. For the model system, as we treat it here in terms of the double harmonic oscillator potential, such environmental contributions are implicitly contained in the values of the force constants which are used for the initial and final states. Thus, one assumes, the experimental values of the force

constants, which are used in the calculation, contain the requisite information about the effect of the environment on the matrix elements for the transfer.

The experimental values of the force constants, however, yield no direct information which can be used to estimate the energy of activation. In order to estimate this energy, it is necessary to resort to the usual collection of models of the solvent; for example, the polar continuum. This problem of the calculation of the energy of activation is important, it was not considered here, but shall be considered in a separate paper.

The model which has been developed in this paper provides a method which can be used to estimate the size of the pre-exponential factors for rate constants for reactions which, one presumes, take place in the diabatic limit. In order to carry out the calculations, one needs only the (observed) frequencies for the vibrations of the transferring species, polarized along the transfer-zxis, in its initial and final states and an estimate of the distance over which the species must migrate. It is not necessary to have complete knowledge of the specific solute-solvent interaction potential energy functions.

As in Part I, this work also clearly indicates that the vibrational overlap between the states involved enters as the principal factor which determines whether a transfer is likely or not. Indeed, both Part I and this work suggest that a simple estimate of the vibrational overlap in the ground state, eqn (19), offers a quick appraisal of the likelihood that a particular configuration (with its specific transfer-distance) can contribute to the rate in a diabatic limit. Such an estimate can be carried out with the use of the quantities a and b which are determined with the use of the experimental frequencies.

This research has been supported in part by a contract with the Office of Naval Research, Arlington, Virginia.

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Figure Caption

The model potential energy for the asymmetric double harmonic oscillator.