a model of geminal repulsions.[25]

Discussion

On balance, the successes of the POS model in simulating molecular orbital computations of potential energy surfaces for bending are far more noteworthy than the failures. Even the difference in hardness of repulsion required to represent the semiempirical EHT fields ($V_{ij} \sim r_{ij}^{-6}$) and ab initio fields ($V_{ij} \sim r_{ij}^{-4}$) is plausible. That EHT yielded the more steeply changing energies is consistent with the fact that its parameterization was frozen instead of being allowed to relax to compensate for shifts in charge accompanying bending deformations. Also satisfying is the fact that the repulsion law accounting for the present AX_4 and AX_6 force fields is the same as that previously needed[4,6] for force fields of AX_5 and AX_7 and, as well, the detailed structure of the latter case[7] (structures of AX_4, AX_5, and AX_6 being independent of the POS law).

While it is gratifying that the POS results agree as well as they do with the molecular orbital calculations, it must be admitted that the present molecular orbital calculations were carried out at a comparatively low level. This was entirely consistent with the exploratory nature of the research. Expensive computations of so many potential constants was hardly warranted before it was learned whether the POS model is worth such an investment. As can be seen in Table II, absolute values of the force constants, which for the EHT depend heavily on K, vary appreciably. Nevertheless, it is important to note that in the dimensionless quantities characterizing the contours of the potential surfaces (Tables III and IV), corresponding molecular orbital and experimental constants are in reasonable agreement with each other.

Clearly, the valence-shell electron-pair repulsion theory in its elementary repelling points-on-a-sphere formulation mimics quantum computations too successfully to be dismissed as spurious. It is apparent that occupied bond orbitals are guided by quantum laws to avoid each other in space. This reluctance to overlap corresponds to a force law that is substantially harder than Coulombic but softer than that corresponding to nonbonded atom–atom repulsions. Moreover, even though atom–atom repulsions would formally give rise to a POS-like field (in the absence of lone pairs), computations of the magnitudes of such repulsions have indicated that they are too small to account for observed harmonic and anharmonic constants.[6,26,27] Empirical evidence, then, tends to corroborate the original rationale of Gillespie and Nyholm[2] who attributed the avoidance to the action of Pauli's principle in the valence shell of the central atom. While this is probably correct as far as it goes, it does not draw attention to the manifestly covalent aspect of the energetics. As pointed out elsewhere,[28] optimization of the aggregate covalent overlap goes hand in hand with the mutual avoidance of the electron-pair bonds. A more definitive theoretical treatment of the underlying principles would be desirable. The case of methane, the simplest of the molecules so far treated yet the most out of step with POS model, serves as a warning against glib generalizations.

Whatever the ultimate explanation and range of applicability of the POS model, it is evident that the model manages to reproduce quite well a large body of information. For this reason it shows promise in a variety of applications. It seems to offer a simple yet more reliable scheme than those frequently adopted by spectroscopists in assigning vibrational frequencies. It can provide quick estimates of anharmonic potential constants for bending if the harmonic constants are known. It yields reasonable treatments of certain dynamic properties of molecules such as Berry pseudororotation in trigonal bipyramids and Pitzer pseudorotation in pentagonal bipyramids.[4,6,26] It was able to account for anomalies in the diffraction patterns of very hot molecules.[8,9] Certainly the valence shell electron pair repulsion theory in its repelling Points-on-a-Sphere representation is much more than a pedagogical aid. It deserves thoughtful consideration by experimentalists and theorists, alike.

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(25) Bartell, L. S.; Fitzwater, S.; Hehre, W. J. *J. Chem. Phys.* **1975**, *63*, 4750.

(26) Bartell, L. S.; Gavin, R. M. *J. Chem. Phys.* **1968**, *48*, 2466.

(27) Rothman, M. J., Bartell, L. S.; Ewig, C. S.; Van Wazer, J. R. *J. Chem. Phys.* **1980**, *73*, 375.

(28) Bartell, L. S. *Inorg. Chem.* **1966**, *5*, 1635.

Intramolecular Proton Exchange in Near Symmetric Cases

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Abstract: We present a simple theoretical model for describing tunnelling of a particle in a symmetric and in an asymmetric double-minimum potential. In the case of an asymmetric double-minimum potential the tunnelling is described by a parameter ρ, which is the ratio between the difference in energy between the particle energies in the two wells and the difference in energy between the lowest two eigenstates E_g and E_u of the corresponding symmetric case. In the asymmetric case, only the fraction $(1 + \rho^2)^{-1}$ of the particle tunnels. The frequency of exchange is increased by a factor $(1 + \rho^2)^{1/2}$ with respect to the corresponding symmetric case.

We have confirmed in a series of calculations[1-3] the well-known result that a particle in a symmetric double-minimum potential will tunnel back and forth between the two wells A and B (Figure 1a). Our calculations give the rate of exchange in intramolecular hydrogen-bonded species such as malonadlehyde[4] and naphthazarin.[5] We also presented evidence that tunnelling is drastically reduced or eliminated when a slight asymmetry is introduced.[2] This evidence was used to explain the strong coupling of the rotation of the methyl group with the rate of proton exchange in

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(1) M. C. Flanigan and J. R. de la Vega, *J. Chem. Phys.*, **61**, 1882 (1974).

(2) J. H. Busch and J. R. de la Vega, *J. Am. Chem. Soc.*, **99**, 2397 (1977).

(3) J. R. de la Vega, *Acc. Chem. Res.*, **15**, 185 (1982).

(4) J. R. de la Vega, J. H. Busch, J. H. Schauble, K. L. Kunze, and B. E. Haggert, *J. Am. Chem. Soc.*, **104**, 3295 (1982).

(5) J. H. Busch, E. M. Fluder, and J. R. de la Vega, *J. Am. Chem. Soc.*, **99**, 2397 (1977).

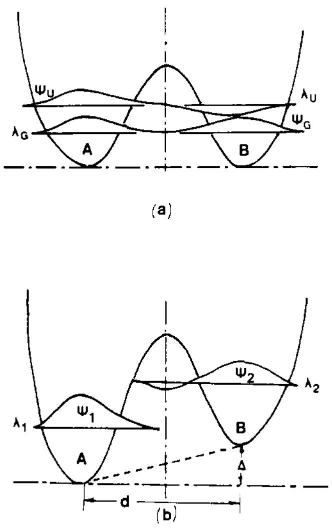

Figure 1. Symmetric (a) and asymmetric (b) double-minimum potentials. The asymmetry in the double-minimum potential may be introduced by adding the term $\Delta x/d$ to the symmetric potential.

α-methyl-β-hydroxyacrolein[6] and the absence of tautomerism in methylnaphthazarin.[5] The above-mentioned systems all have a tunnelling barrier of 10 kcal/mol or more and the introduction of a perturbation causing a small difference in energy between the minima quenches tunnelling. More recently, we have found that for 9-hydroxyphenalen-1-one, which has a tunnelling barrier of 5.25 kcal/mol,[7] a small difference in energy between the minima reduce tunnelling without eliminating it.[7-9]

The question of tunnelling in symmetric double-minimum potentials was considered quantum mechanically as early as 1933 in the study of the microwave spectrum of ammonia.[10]

In the symmetric case, tunnelling is given by the frequency of exchange between the wells. In this case, the proton must spend equal amounts of time in each well because of symmetry.

In the asymmetric case, tunnelling is more complex. Obviously, the proton will not spend equal amounts of time in each well when the potential is no longer symmetric. The motion of a proton in an asymmetric double-minimum potential was studied by Brickmann and Zimmermann[11] and also by Flanigan and de la Vega[1] by means of rather elaborate calculations. We will show in this paper that the main features of tunnelling in the case of an asymmetric potential may be represented by means of a relatively simple model. In our model the main features of proton exchange in an asymmetric double-minimum potential may be expressed in terms of parameters directly related to experimental quantities. Our theoretical results predict both a quenching of tunnelling due to changes in probability amplitudes and a change in the tunnelling frequency of exchange between the two wells. In previous studies the effect of the asymmetry was limited to the change in tunnelling frequency.

Theory

We consider a particle in a double-minimum potential, either symmetric as in Figure 1a or asymmetric Figure 1b. We represent the situation where the particle is in well A by a wave function ϕ_A and the situation where the particle is in well B by a wave function ϕ_B. Obviously, we consider lowest eigenstates of the system only.

In the symmetric case, the Hamiltonian $\mathcal{H}_0$ is symmetric and the matrix elements are given by

$$H_{AA} = \langle \phi_A | \mathcal{H}_0 | \phi_A \rangle = H_{BB} = \langle \phi_B | \mathcal{H}_0 | \phi_B \rangle = E$$
$$H_{AB} = \langle \phi_A | \mathcal{H}_0 | \phi_B \rangle = H_{BA} = \langle \phi_B | \mathcal{H}_0 | \phi_A \rangle = \delta \qquad (1)$$

It is easily verified that the corresponding eigenvalues and eigenfunctions are

$$\begin{aligned} E_g &= E + \delta \qquad \Psi_g = (1/\sqrt{2})(\phi_A + \phi_B) \\ E_u &= E - \delta \qquad \Psi_u = (1/\sqrt{2})(\phi_A - \phi_B) \end{aligned} \qquad (2)$$

The particle will tunnel back and forth between the wells with the frequency $\omega_0 = 2\delta/\hbar$ if it is located initially in well A or well B.

We now consider the asymmetric case by introducing a perturbation H' having the following matrix elememts

$$\begin{aligned} \langle \phi_A | H' | \phi_A \rangle &= -\langle \phi_B | H' | \phi_B \rangle = \tfrac{1}{2}\Delta = \rho\delta \\ \langle \phi_A | H' | \phi_B \rangle &= \langle \phi_B | H' | \phi_A \rangle = 0 \end{aligned} \qquad (3)$$

In our model the perturbation is defined by means of the above matrix elements, but we may visualize that H' is represented by an analytical expression

$$H' = \Delta \frac{x}{d} \qquad (3')$$

where Δ is the energy difference between the potential minima in wells A and B and d is the distance between the two potential minima and x is the coordinate.

In our model, ρ is the asymmetry parameter and it will prove to be convenient to write ρ as

$$\rho = tg\alpha \qquad -\frac{\pi}{2} \leq \alpha \leq \frac{\pi}{2} \qquad (4)$$

The eigenvalues and eigenfunctions of the perturbed system are derived by diagonalizing the corresponding 2 × 2 matrix. The eigenvalues λ_2 and λ_2 are

$$\lambda_1 = E + (\delta/\cos\alpha) \qquad \lambda_2 = E - (\delta/\cos\alpha) \qquad (5)$$

and the corresponding eigenfunctions Ψ_1 Ψ_2 are

$$\begin{aligned} \Psi_1 &= (2 + 2\sin\alpha)^{-1/2}[(1 + \sin\alpha)\phi_A + \cos\alpha\phi_B] \\ \Psi_2 &= (2 + 2\sin\alpha)^{-1/2}[\cos\alpha\phi_A - (1 + \sin\alpha)\phi_B] \end{aligned} \qquad (6)$$

The general time-dependent wave function of a particle in the perturbed asymmetric double-minimum potential is

$$\Psi(t) = c_1\Psi_1 \exp(-i\lambda_1 t/\hbar) + c_2\Psi_2 \exp(-i\lambda_2 t/\hbar) \qquad (7)$$

We now consider the situation where the particle is in well A at time $t = 0$, or

$$\Psi(0) = \phi_A \qquad (8)$$

Then the coefficients in eq 7 are

$$\begin{aligned} c_1 &= \langle \Psi_1 | \phi_A \rangle = (2 + 2\sin\alpha)^{-1/2}(1 + \sin\alpha) \\ c_2 &= \langle \Psi_2 | \phi_A \rangle = (2 + 2\sin\alpha)^{-1/2}\cos\alpha \end{aligned} \qquad (9)$$

and the function $\Psi(t)$ becomes

$$\Psi(t) = \tfrac{1}{2}\exp(-iEt/\hbar) \times \{[(1 + \sin\alpha)e^{-i\omega t} + (1 - \sin\alpha)e^{i\omega t}]\phi_A + \cos\alpha\,[e^{-i\omega t} + e^{i\omega t}]\phi_B\} \qquad (10)$$

where

$$\hbar\omega = \delta/\cos\alpha \qquad (11)$$

The probability density function is easily derived from eq 10

$$\Psi^*(t)\Psi(t) = P_A\phi_A{}^*\phi_A + P_B\phi^*\phi_B + P_{AB}\phi^*{}_A\phi_B + P_{AB}{}^*\phi_A\phi_B{}^* \qquad (12)$$

where

$$P_A = 1 - \cos^2\alpha\sin^2\omega t \qquad P_b = \cos^2\alpha\sin^2\omega t \qquad (13)$$

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[6] R. Rossetti, R. C. Haddon, and L. E. Brus, *J. Am. Chem. Soc.*, **102**, 6913 (1980).

[7] L. M. Jackman, private communication.

[8] R. Rossetti, R. Rayford, R. C. Haddon, and L. E. Brus, *J. Am. Chem. Soc.*, **103**, 4303 (1981).

[9] K. L. Kunze and J. R. de la Vega, *J. Am. Chem. Soc.* **1984**, *106*, 6528.

[10] R. P. Bell, "Proton Tunnelling in Chemistry", Chapman and Hall, London, 1981.

[11] J. Brickman, and H. Zimmerman, *J. Chem. Phys.*, **50**, 1608 (1969).

J. Am. Chem. Soc. **1984**, *106*, 7705–7710

Table I. Values of the Energy Differences Δ between the Minima and of the Energy Differences between the Gerade–Ungerade States in au[a]

	ref	Δ	δ	ρ	P_B(max)
methyloxonium ion	2	4.054×10^{-4}	1.626×10^{-5}	24.0	0.0017
α-methyl-β-hydroxyacrolein	5	8.400×10^{-4}	9.257×10^{-5}	9.130	0.0110
2-methylnaphthazarin	4	1.430×10^{-3}	1.530×10^{-9}	930000.0	0.0000
9-hydroxyphenalen-1-one	9	7.355×10^{-4}	4.810×10^{-4}	1.529	0.3000

[a] We also list values of the asymmetry parameter ρ and of P_B(max) for various molecules.

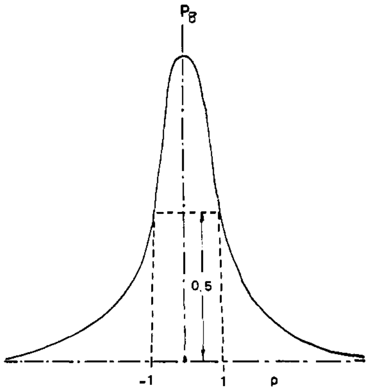

Figure 2. Plot of the probability P_B of finding the proton at time $t = \pi/2\omega$ as a function of the asymmetry parameter $\rho = \Delta/2\delta$. The half-width of the Lorentzian curve corresponds to $\rho = 1$.

Discussion

The coefficients P_A and P_B of eq 13 represent the probabilities of finding the proton either in well A or in well B, respectively. At time $t = 0$, the particle is in well A. The maximum probability of finding the particle in well B is

$$q = P_B(\max) = \cos^2 \alpha = 1/(1 + \rho^2) \qquad (14)$$

and it occurs when $\omega t = (n + {}^1/_2)\pi$.

Equation 13 presents a clear and simple description of the effect of the perturbation on tunnelling. It is easily seen that only the fraction q defined by eq 14 will tunnel. The fraction q is a Lorentzian with half-width equal to unity which we have sketched in Figure 2.

It should be noted that the frequency of exchange between the wells increases with the asymmetry of the potential. From eq 5 it follows that this frequency is given by

$$h\nu = 2\delta\,(1 + \rho^2)^{1/2} \qquad \nu/\nu_0 = (1 + \rho^2)^{1/2} \qquad (15)$$

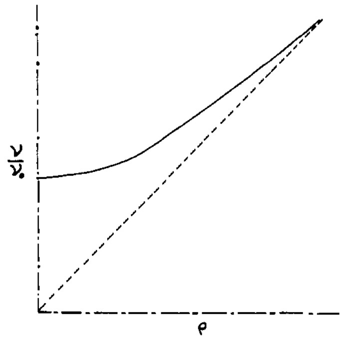

Figure 3. Ratio of the frequencies ν and ν_0 as a function of the asymmetric parameter ρ. The frequency ν increases with the asymmetry of the double-minimum potential.

In Figure 3 we represent the frequency ν as a function of the asymmetry parameter ρ.

It is worth noting that our eq 15 predicts an increase in the tunnelling frequency with increasing ρ. This is reasonable because the effect of the perturbation is always an increased separation of the two lowest energy levels and consequently the effect of the perturbation should cause an increase of the exchange frequency. We used eq 14 to describe the various systems that we studied previously[2-5,9] and we present the results in Table I. For methyloxonium ion and α-methyl-β-hydroxyacrolein the probability of finding the proton in well B is decreased by 3 and 2 orders of magnitude while in the case of 2-methylnaphthazarin tunnelling is completely eliminated. These results are consistent with the interpretation of current experimental data and with our previously published theoretical calculations. The result for 9-hydroxyphenalen-1-one is consistent with the currently available experimental evidence; it is identical with that calculated from the eigenstates of the asymmetric double-minimum potential by the variational method with a large basis set,[9] where the probability of tunnelling is obtained by numerical integration of the wave function in well B at time $t = \pi/2\omega$.

Intermolecular Pyrene Excimer Formation in Zeolites. Decay Parameters and Ground-State Association

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Abstract: Pyrene has been introduced into various zeolites in order to observe whether monomer or excimer formation dominates. Evidence has been found for ground-state association of pyrene, deposition of pyrene microcrystallites on external zeolite surfaces, and monomers and excimers inside the supercages of large-pore zeolites. The preparation of the materials controls what types of species will exist. Excimers in the supercages only exist if the zeolite has been dehydrated first. Solvents of varying polarity affect the luminescence in the monomer region. Quenching studies with Cs^+ ions and halonaphthalenes indicate that ground-state associated species can be dissociated. Luminescence lifetime, X-ray powder diffraction, and Fourier transform infrared experiments lend support to assignments of excimers, monomers, and ground-state-associated species and whether these are in internal or external sites.

The photochemical and photophysical behavior of fluorescent probes on solid surfaces has been sparsely studied. In recent years progress in this area has been made due to careful studies of well-defined supports, simple fluorescent probes, and molecular interactions. Pyrene has been used in several of these studies because the quantum yield of emission is high, the molecular

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