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Dynamic potential barrier effects in hydrogen tunneling in trans–cis isomerizations

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A simple model is employed to illustrate the influence of the dynamic effective potential resulting from torsional motion on tunneling via bending modes in trans–cis isomerization in polyatomic molecules. We show that the effect is significant and can determine the dominant tunneling mode in systems such as HSiOH.

1. Introduction

Most treatments of barrier tunneling make use of simplifying assumptions, such as one-dimensional paths. As chemists,we are often interested in processes that occur in polyatomic molecules, thus the tunneling processes of interest are often multi-dimensional. Makri and Miller [1] have presented a method for treating tunneling in multi-dimensional systems semiclassically. However, it is often necessary and appropriate to calculate tunneling corrections by assuming that it occurs along some special "tunneling direction", for example, along a normal mode direction.

An example where this approach may be reasonable is trans–cis isomerization. It is often a good approximation to treat the torsional motion as separable. However, as ab initio calculations have shown, trans–cis isomerization can occur via an angle bending mode in some molecules. The purpose of this Letter is to point out that there are dynamic effects which arise from the torsional motion that must be taken into account for tunneling along a bending mode direction. We use a very simple model to illustrate the qualitative effects of the torsional motion on the bending mode tunneling. We consider the simplest case, that is, a four-atom molecule, namely, HSiOH.

The cis and trans conformers of HSiOH, and its isotopic (D and ^{18}O) analogs, have received a lot of attention lately. Ismail et al. [2] studied the interaction of silicon atoms and water molecules in a solid argon matrix. Infrared spectra of the products (including cis and trans conformers of HSiOH, HSi^{18}OH, HSiOD, and HSi^{18}OD) were measured and assigned. Withnall and Andrews [3] studied the matrix reactions of silane and oxygen atoms and identified HSiOH, HSi^{18}OH, DSiOD, and DSi^{18}OD by infrared absorption. Kudo and Nagase [4,5] have reported ab initio calculations for H_2SiO and related molecules, including trans- and cis-HSiOH. They found that there are two possibilities for the trans to cis isomerization transition state: either along an in-plane bending mode or along the torsional direction. Their results showed that the latter, which has a barrier of 11 kcal/mol, is 1.1 kcal/mol lower than the former. Sakai and Jordan [6] have reported SCF results for the structures, stabilities, and normal mode frequencies for cis- and trans-HSiOH. (They also reported results for similar molecules. They found that the lowest energy path for trans→cis isomerization in HAlOH involves the in-plane motion of the H-atom bonded to the O-atom rather than the torsional motion as in the case of HBOH, HCOH, and HSiOH.) Tachibana et al. [7,8] have investigated

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tunneling in the cis–trans isomerization in HSiOH by using an ab initio IRC (intrinsic reaction coordinate) method. They proposed that the isomerization path may be regarded as one-dimensional along the direction of the SiOH bending mode. That is, the path maintains C_s symmetry and the vibrational modes orthogonal to it do not contribute to the dynamics along the path.

We should also point out some classical dynamics studies that are relevant to this problem. Spears and Hutchinson [9,10] used classical mechanics to study the dynamics of vibrationally excited trans-diimide. Using a very simple model and classical trajectory calculations, they showed that the isomerization dynamics of diimide are dominated by the "fictitious" forces arising from the presence of torsional motion and the source of the final "kick" of energy into the isomerization coordinate (torsion) arises from a Coriolis coupling of the torsion to the NH stretches. They pointed out that the isomerization via a planar bending mechanism is prevented since such motion entails crossing an infinite effective potential due to the centrifugal force. That is, they concluded that the bending pathway is inactive.

We focus here on the dynamic effects on tunneling paths between the trans and cis conformers of molecules of the type HABC, taking HSiOH as an example. We use a simple model to illustrate the effect of the dynamic effective potential, which arises from the torsional motion, on the tunneling probability. It is pointed out that this "dynamic" correction to the "static" potential in one-dimensional treatments of tunneling for cis–trans isomerizations may be important. We also note that due to the existence of this dynamic effect, the realistic tunneling path may be a curved route that is a combination of the torsional and bending modes, and is possibly coupled with the stretching modes as well.

2. The dynamic effective potential barrier

The Born–Oppenheimer approximation allows the Schrödinger equation for a molecule to be separated into two equations,

$$(T_e + V_{ee} + V_{en} + V_{nn})\Psi_e(\boldsymbol{R}, \boldsymbol{r}) = E(\boldsymbol{R})\Psi_e(\boldsymbol{R}, \boldsymbol{r}) , \qquad (1)$$

$$[T_n + E(\boldsymbol{R})]\Psi_n(\boldsymbol{R}) = \epsilon\Psi_n(\boldsymbol{R}) , \qquad (2)$$

where $\psi_e(\boldsymbol{R}, \boldsymbol{r})$ and $\psi_n(\boldsymbol{R})$ are the electronic and nuclear wavefunctions, respectively, $\boldsymbol{R}$ and $\boldsymbol{r}$ are the position vectors of the nuclei and electrons, respectively; T_e, T_n, V_{ee}, V_{en}, and V_{nn} are the operators for the kinetic energies for the nuclei and electrons, electron repulsions, electron–nuclear attractions, and nuclear repulsions, respectively; ϵ is the total energy and $E(\boldsymbol{R})$ is the "potential energy surface" (which we refer to as the static potential).

Now, let us consider the trans→cis isomerization in HABC-type molecules taking HSiOH as an example. The ab initio calculations [4,7] show that the trans- and cis-HSiOH conformers exist in local minima with planar structures on the ground-state potential energy surface. The two minima are separated by barriers of about 10 kcal/mol along both the out-of-plane torsional coordinate and the in-plane bending mode direction. Kudo and Nagase [4] and Sakai and Jordan [6] have suggested that the torsional mode is the dominant pathway for the isomerization. However, Tachibana et al. [7,8] assumed that the isomerization involves pure SiOH bending motion and computed tunneling probabilities for passage through the barrier along that coordinate. The dominant pathway for the isomerization is determined simply by the relative heights of the two barriers on the static potential energy surface. In the following, we just show that the effective potential, which arises from dynamic effects, should be considered for this process.

The coordinate system for our model is illustrated in fig. 1. The SiO bond is along the z axis with the O-atom at the origin. Points A, B, C, D, and E are all located on a sphere of radius R_0, the equilibrium OH bond length. The equilibrium cis and trans geometries both lie in the YOZ plane. The OH bond points to the upper right for the trans geometry and the upper left for the cis. As the molecular translation and rotation are separated out, the static potential can be written generally as $V(r_1, r_2, \theta_1, \theta_2, \varphi_1 - \varphi_2)$, where r_1, θ_1, and φ_1 describe the first H-atom, and r_2, θ_2, and φ_2 the second. The torsional potential depends only on the difference $\varphi_1 - \varphi_2$.

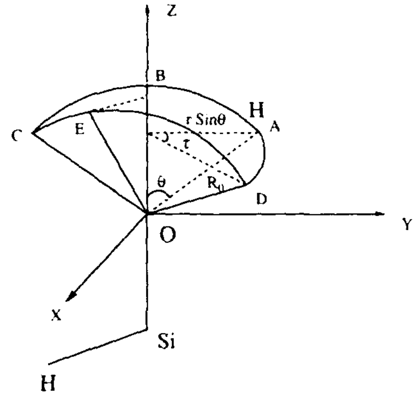

Fig. 1. Illustration of the coordinates for the model. All atoms are in the YOZ plane at the cis and trans equilibrium geometries. The points A, B, C, D, and E represent points along the isomerization pathways, where A and C are the trans and cis conformers, respectively. Path A→B→C is the pure in-plane bending mode isomerization. Passage through point E involves a combination of SiOH bending and torsional motion.

The torsional motion involves rotation of the two hydrogen atoms about the z axis. The z component L_z of the total internal angular momentum L is

$$L_z = L_{1z} + L_{2z} , \tag{3}$$

where the subscripts 1 and 2 indicate the two hydrogens. The potential commutes with L_z,

$$[V(r_1, r_2, \theta_1, \theta_2, \varphi_1 - \varphi_2), L_z] = 0 , \tag{4}$$

i.e. L_z is a constant of the motion in the ground state for which the eigenvalue of L_z is zero since the total rotation has been separated out. However, the operator

$$L^2 = L_x^2 + L_y^2 + L_z^2 \tag{5}$$

is not a constant of the motion, that is,

$$[V(r_1, r_2, \theta_1, \theta_2, \varphi_1 - \varphi_2), L^2] \neq 0 . \tag{6}$$

From symmetry considerations of group theory, $V(r_1, r_2, \theta_1, \theta_2, \varphi_1 - \varphi_2)$ is invariant under rotation about the z axis since φ_1 becomes $\varphi_1 + \varphi$ and φ_2 becomes $\varphi_2 + \varphi$ as the system rotates by an angle φ about the z axis. Thus, V should commute with the operator L_z since the infinitesimal rotation operator about the z axis is $1 - \mathrm{i}\epsilon L_z$, where ϵ is the infinitesimal rotation angle. Or directly, given a function $\Psi(r_1, r_2, \theta_1, \theta_2, \varphi_1, \varphi_2)$, it is easy to verify that $(VL_z - L_zV)$, since $L_z = L_{1z} + L_{2z} = -\mathrm{i}\hbar\partial/\partial\varphi_1 - \mathrm{i}\hbar\partial/\partial\varphi_2$ and we have $L_zV = 0$. From this it is clear that L_x and L_y, and thus L^2, do not commute with the potential V. Thus, the L^2 operator has a distribution of values rather than a definite eigenvalue for the internal nuclear motion of HABC in the ground state.

Now, let us return to our model as illustrated in fig. 1. Since the torsional motion (τ in fig. 1) is an internal rotation about the SiO bond in HSiOH, we can regard the HSi bond fixed in the YOZ plane and thus consider only the relative rotation of the H-atom bonded to O-atom. When this H-atom moves from point A to C in fig. 1, the geometry changes from trans to cis. The H-atom moving along a certain path s around the sphere experiences a dynamic effective potential V_{dyn} due to torsional motion,

$$V_{\mathrm{dyn}} = L^2/2\mu(r\sin\theta)^2 , \tag{7}$$

where μ is the mass of the H-atom and the other quantities are as defined in fig. 1. This comes from the kinetic energy operator T_{n} of eq. (2). Thus, the bending motion of the H-atom is coupled to the torsional motion such that it cannot be treated as purely one-dimensional on the static potential energy surface.

In this simple model, motion along the reaction coordinate s and torsional direction x is considered in the kinetic energy operator T_{n}. Along a given tunneling path $T_{\mathrm{n}} = \frac{1}{2}(p_s^2 + p_x^2) + T_{sx} + V(s)$, where $\frac{1}{2}p_s^2$ and $\frac{1}{2}p_x^2$ are kinetic energy operators along s and x, respectively. T_{sx} is the coupling of the two motions, and $V(s)$ is the potential energy along the s. Here, we only want to explore the dynamic effect due to the torsion so we ignore the coupling term T_{sx}. The $\frac{1}{2}p_x^2$ term is represented by $L^2/2\mu(r\sin\theta)^2$, where $r\sin\theta$ is the distance from the H-atom to the z axis and r is the OH bond length. In more accurate treatments, such as those by Marcus [11] and Miller et al. [12], the reaction path Hamiltonian can be written (considering only the coordinates s and x) as

$$H = \frac{1}{2}\frac{p_s^2}{[1 + \kappa(s)x]^2} + \tfrac{1}{2}p_x^2 + V_0(s) + V_1(s, x) ,$$

where $\kappa(s)$ is the curvature of the path s, x is the distance deviated normal to s, $V_0(s)$ is the potential along the path, and $V_1(s, x)$ is the potential change as the motion deviates from the path s. At $x = 0$, i.e.

along the reaction coordinate s, $V_1(s, x)=0$ and $K(s)x=0$, which leads to eq. (7).

It should be noted that the case we treat, the effect of torsional motion on the tunneling path, is different to those usually considered [11,12]. The usual treatment is for vibrational modes that are normal to the path s with a harmonic or modified-harmonic model, and where the vibrational energy only about the path s is considered.

Let us now make a rough estimate of the effect of the dynamic effective potential on the tunneling path in the trans→cis isomerization of HSiOH. We refer again to fig. 1, which illustrates isomerization along the pathways with torsional motion. When the hydrogen atom is at point A $\tau=0$ and $\theta=65.5°$, at point B τ is undefined and $\theta=0°$, at point C $\tau=180°$ and $\theta=65.5°$, at point D τ is between 0° and 90° and $\theta=65.5°$, and at point E $\tau=90°$ and $\theta<65.5°$. Pure planar isomerization is along the path ABC. The more general path involves a torsion plus bend motion as illustrated by the points ADEC in fig. 1, where it is visualized as being broken down into simple segments of the two motions. We can roughly estimate this path by assuming it follows the smallest polar angle $\theta=(65.5°/90°)\,\tau$ as the atom moves from A to C. Quantum mechanically, the internal rotation operator L^2 has an average deviation (uncertainty) on the order of $\hbar^2$. Thus, the dependence of the largest value of the dynamic effective potential along the path on τ can be expressed approximately as

$$V'_{\text{dep}}(\tau)\sim\hbar^2\left[2\mu R_0^2\sin^2\left(\frac{65.5°}{90°}\,\tau\right)\right]^{-1}$$
$$=0.05\sin^{-2}(0.73\tau)\ \text{kcal/mol}\,. \qquad (8)$$

The cis and trans conformers are at about the same energy and the barriers for the two isomerization channels on the static potential energy surface are roughly at the same level (about 10 kcal/mol above the conformer wells). We approximate the barrier height of the total effective potential as

$$V'_0(\tau)=[10.0+0.05\sin^{-2}(0.73\tau)]\ \text{kcal/mol}\,, \qquad (9)$$

in order to simply show the dynamic effect. The dependence of $V'_0(\tau)$ on τ is plotted in fig. 2. It decreases rapidly as the torsional angle increases.

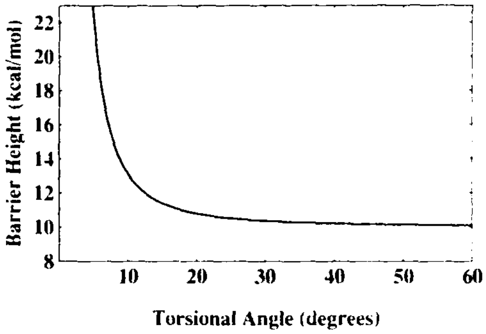

Fig. 2. The barrier height of the approximate effective potential as a function of the torsional angle τ, eq. (9).

3. Tunneling probability

To estimate the effect of the dynamic effective potential on the tunneling, we represent the potential with the Eckart barrier [13],

$$V(s)=V'_0(\tau)\,\text{sech}^2(s)\,, \qquad (10)$$

where s is the tunneling coordinate. Fig. 3 shows the shapes of the potential barrier for a few τ, where the lowest one is the static potential.

The one-dimensional Schrödinger equation along the tunneling path,

$$\frac{d^2\psi(s)}{ds^2}+\frac{2m}{\hbar^2}[E-V'_0\,\text{sech}^2(s)]\psi(s)=0\,. \qquad (11)$$

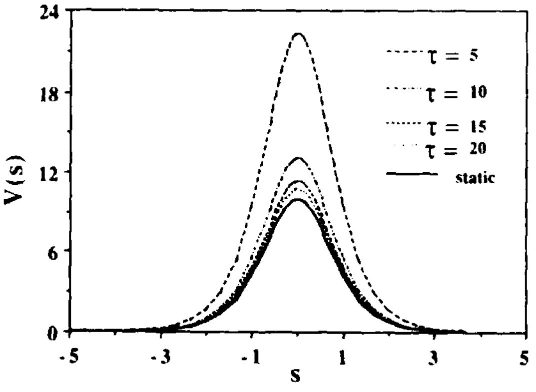

Fig. 3. The Eckart barriers used to represent the static potential and the dynamic effective potentials for torsional angles $\tau=5°$, 10°, 15°, and 20°.

can be solved analytically [13]. The permeability is

$$P_{\mathrm{tun}}=\sinh^2(\pi k)\times[\sinh^2(\pi k)+\cosh^2\sqrt{\tfrac{1}{2}\pi(8mV_0/\hbar^2-1)}]^{-1}, \tag{12}$$

where

$$k=\sqrt{2mE}/\hbar .$$

The dependence of tunneling probability P_{tun} on the torsional angle τ for $E=8$ kcal/mol is shown in fig. 4. The probability of tunneling is zero at $\tau=0$ since the total effective potential is infinite. As τ increases V_{dep} decreases rapidly (see fig. 2) and the tunneling probability becomes significant at about $\tau=20°$.

The torsional energy levels are, of course, quantized with relatively large spacings. We have not considered the quantized levels here, although one could easily do so. We merely wish to illustrate the effect and thus have considered the trans–cis motion on a potential energy surface where the torsional mode might be considered to be any state, generally, not an eigenstate of the torsion.

We have ignored the effects of the variation in the width of the barrier, which is certainly significant. We have assumed that all paths have the same width since we are interested in merely illustrating the qualitative dynamic effect of the torsional motion on the tunneling paths. Work is in progress on a more accurate and elaborate treatment of this problem.

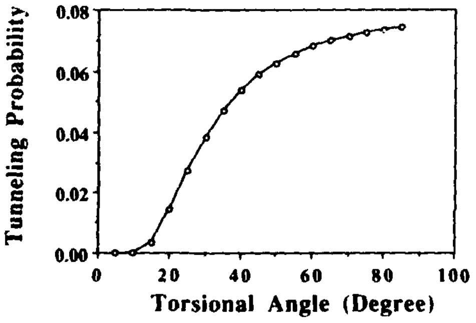

Fig. 4. The tunneling probability as a function of the torsional angle.

4. Conclusions

We have used a simple model to illustrate the effect of the dynamic effective potential that results from torsional motion on tunneling paths along the trans→cis isomerization coordinate. This effect may be important in many systems and must be explicitly considered in one-dimensional treatments of tunneling. Because of this effect, the torsional or a curved torsional-plus-bend pathway, possibly coupled to stretching, is likely to be preferred over the pure in-plane bending pathway.

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