A Semiclassical Study of Tunneling Effects in Aziridine

by Yin Guo, Angela K. Wilson, Cary F. Chabalowski, and Donald L. Thompson

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A Semiclassical Study of Tunneling Effects in Aziridine

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Abstract

The tunneling effects in the molecular inversion of aziridine are investigated. A full-dimensional potential was constructed based on ab initio results and used to study the effect of vibrational excitations on tunneling. Using the semiclassical approach that incorporates tunneling into classical trajectory calculations, it is found that excitations of all the modes except the reaction coordinate have negligible effects on tunneling. This allows accurate thermal-rate calculations carried out by using a one-dimensional (1-D) model. (This is in accord with the conclusions of the work by N. Rom, V. Ryaboy, and N. Moiseyev [Chemical Physics Letters, vol. 204, p. 175, 1993] and by Z. Smedarchina, W. Siebrand, and M. Z. Zgierski [Journal of Chemical Physics, vol. 102, p. 7024, 1995].) A 1-D Weutzl-Kramers-Brillouin (WKB) formula was employed to obtain the level splitting and was found to be very accurate based on comparisons with the quantum results. Furthermore, the calculated thermal rates are in good agreement with the experimentally measured values. The results provide insight into the reaction mechanism and explanations for the experimental findings of non-Rice-Ramsperger-Kassel-Marcus (RRKM) behavior and incoherent tunneling.
Acknowledgments

This work was supported by the U.S. Army Research Office (ARO), Grant No. DAAG55-98-1-0089.
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1. Introduction

The intramolecular conversion in aziridine (see Figure 1) has been extensively studied both experimentally and theoretically [1–5]. Of particular interest is the finding by Borchardt and Bauer [1]: the observed inversion rate constants do not depend on pressure over the range of 5–1,100 torr for temperatures from 298–388 K, while standard Rice-Ramsperger-Kassel-Marcus (RRKM) calculations indicate that the system should be in the bimolecular regime for pressures below 100 torr. This non-RRKM behavior was attributed to the slow internal vibrational relaxation (IVR) in this molecule—the rate of reaction is limited by the rate of IVR [1].

![Figure 1. Schematic Illustration of Molecular Inversion in Aziridine.](image)

The purpose of this paper is to provide a comprehensive study of the inversion dynamics of aziridine to gain insight about the reaction mechanism. Of main interest is in the tunneling effects in this reaction. Since the migrating atom is hydrogen and the experimental temperatures are near 300 K, appreciable tunneling effects are expected. The method employed here is the multidimensional semiclassical approach that has been used for unimolecular and bimolecular reactions [6–13], which incorporates tunneling within classical trajectory simulations and, thus, allows for explicit treatment of the full-dimensional dynamics.

There are already some theoretical studies on tunneling in aziridine [4, 5] in which a one-dimensional (1-D) potential along the reaction coordinate [4] or an adiabatic 1-D potential that includes the effects of high-frequency modes [5] is used. Rom, Ryaboy, and Moiseyev [4]
treated the effect of other degrees of freedom by introducing an absorbing potential. They also performed calculations using a two-dimensional (2-D) potential, which includes the N–H stretch mode, and obtained good agreement with the results from the 1-D calculations. Both studies [4, 5] yielded good agreement with the experimental thermal rates, suggesting that a 1-D treatment is adequate. The multidimensional semiclassical approach enables direct verification of this point by explicitly investigating the dynamic motions of all the atoms and their effects on tunneling.

The physical quantity of interest is the thermal-rate constant, for which experimental results for both the normal and deuterated species are available [2]. In principle, it can be calculated by the standard expression

\[ k(T) = \frac{\sum_n k_n \exp\left(-\frac{E_n}{k_B T}\right)}{\sum_n \exp\left(-\frac{E_n}{k_B T}\right)}, \]

where \( E_n \) is the total energy of the molecule in a specified state with quantum numbers \( n = \{n_1, n_2, \ldots\} \), and \( k_n \) is the reaction probability for that state. However, the number of terms in the sum can be quite large as the energy increases, making the computation prohibitively expensive. With the use of the multidimensional semiclassical approach, it is explicitly demonstrated, by selectively exciting each mode, that there is only one mode that plays a dominant role in the tunneling. Thus, the thermal-rate calculation reduces to a much simpler 1-D problem. Since the reaction probability for a given energy would be independent of the excitation site if the system were statistical, these mode-selective results also provide insight into the observed non-RRKM behavior.

Besides the apparent non-RRKM behavior, another interesting aspect of the system is the incoherent tunneling, (i.e., the reaction is characterized by rate processes). For a symmetric double-well potential, it is usually expected that the molecular motions are coherent oscillations between the wells rather than rate processes and that the oscillating frequency is proportional to the level splitting. A rate process occurs in a double-well system only when there is some
damping mechanism that broadens the energy levels. If this broadening exceeds the level splitting, then tunneling becomes irreversible. In the present case, since the measured rates [1] show no pressure dependence, the intermolecular collisions should not be the major cause of the broadening. The other possible cause, as suggested by Smedarchina, Wiebrand, and Zgierski [5], is the intramolecular couplings; the density of states and the anharmonicity increase rapidly as the energy increases, which may lead to greater broadening than splitting for high energy states. The results here are in agreement with those of Rom, Ryaboy, and Moiseyev [4]: the level splittings of the low-energy states are too small to be observed, and the states contributing to the measured thermal rates are those near the barrier top. Thus, rate constants rather than level splittings were observed in the experiments [1, 2].

This paper is organized as follows. The potential energy surface is described in section 2, the semiclassical method for computing thermal rates in section 3, the results and discussions in section 4, and the conclusions in section 5.

2. Potential Energy Surface

The potential energy surface used in this study is based on a valence force field with the normal-mode frequencies fitted to ab initio results calculated using the Gaussian 94 codes [14]. Both the equilibrium and transition states are calculated at the MP2 [15] level with the frozen core approximation using the 6-311G/(2df, 2p) [16–19] basis set. The functional form of the total potential is

\[ V = S_1(\phi) V_A + [I - S_1(\phi)] V_B + V(\phi). \] (2)

Here, \( \phi \) is the reaction coordinate (the NH wag angle), \( V(\phi) \) is a double-well potential along \( \phi \), \( V_A \) and \( V_B \) consist of the terms corresponding to the two isomers, and \( S_1(\phi) \) is a switching function that smoothly connects \( V_A \) and \( V_B \), that is,
\[ S_1(\phi) = \frac{1}{2} [1 + \tanh(a\phi)] , \quad (3) \]

where \( a \) is chosen to be 3.0 rad\(^{-1}\).

The double-well potential \( V(\phi) \) is of the form

\[ V(\phi) = C_0 + C_2 \phi^2 + C_4 \phi^4 , \quad (4) \]

where \( C_0 = 19.2 \text{kcal/mol} \) and is the barrier height, and \( C_2 \) and \( C_4 \) are 27.1 and 9.57 rad\(^{-4}\)kcal/mol, respectively, determined by requiring \( V(\phi) \) and its first derivative at the equilibrium NH wag angle (68.2\(^\circ\)) to be zero.

Each of the potentials, \( V_A \) and \( V_B \), is a sum of Morse functions for bond stretches, harmonic functions for the angle-bending terms, and three-term cosine expansions for the dihedral interactions, that is,

\[ V_{A,B} = V_{\text{stretch}} + V_{\text{bend}} + V_{\text{dihedral}} , \quad (5) \]

where

\[ V_{\text{stretch}} = \sum_i D_i \left[ 1 - \exp \left[ -\beta (r_i - r_i^0) \right] \right]^2 , \quad (6) \]

\[ V_{\text{bend}} = \sum \frac{1}{2} k_i \left( \theta_i - \theta_i^0 \right)^2 , \quad (7) \]

and

\[ V_{\text{dihedral}} = \sum_i [a_{i0} + a_{i2} \cos (2\tau) + a_{i4} \cos (4\tau)] . \quad (8) \]

The values of the parameters in equations (6)–(8) are given in Table 1. The equilibrium CNH angles used in the bending potential are also functions of the reaction coordinate.
Table 1. Potential Energy Surface Parameters

<table>
<thead>
<tr>
<th>Bond</th>
<th>$r^0$ (Å)</th>
<th>D (kcal/mol)</th>
<th>$\beta$ (Å$^{-1}$)</th>
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</thead>
<tbody>
<tr>
<td>N–H</td>
<td>1.014</td>
<td>99.77</td>
<td>2.135</td>
</tr>
<tr>
<td>C–C</td>
<td>1.478</td>
<td>54.73</td>
<td>1.966</td>
</tr>
<tr>
<td>C–N</td>
<td>1.473</td>
<td>45.89</td>
<td>2.678</td>
</tr>
<tr>
<td>C–H'</td>
<td>1.079</td>
<td>110.61</td>
<td>1.826</td>
</tr>
<tr>
<td>C–H''</td>
<td>1.080</td>
<td>110.61</td>
<td>1.825</td>
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<table>
<thead>
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<th>Angle</th>
<th>$\theta^0$ (°)</th>
<th>$k$ (kcal/mol rad$^2$)</th>
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<tbody>
<tr>
<td>HNC</td>
<td>108.75</td>
<td>74.32</td>
</tr>
<tr>
<td>NCC</td>
<td>59.90</td>
<td>113.45</td>
</tr>
<tr>
<td>CNC</td>
<td>60.21</td>
<td>183.18</td>
</tr>
<tr>
<td>NCH''</td>
<td>118.32</td>
<td>77.78</td>
</tr>
<tr>
<td>NCH'</td>
<td>114.33</td>
<td>99.61</td>
</tr>
<tr>
<td>CCH''</td>
<td>117.77</td>
<td>94.23</td>
</tr>
<tr>
<td>CCH'</td>
<td>119.53</td>
<td>100.89</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Dihedral Angle</th>
<th>$\tau^0$ (°)</th>
<th>$a_0$ (kcal/mol)</th>
<th>$a_2$ (kcal/mol)</th>
<th>$a_4$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H'CCH''</td>
<td>149.04</td>
<td>1.738</td>
<td>-2.267</td>
<td>1.204</td>
</tr>
</tbody>
</table>

\[
\theta(\phi) = \theta_{eq} - (\theta_{eq} - \theta_{ts}) \exp (-b \phi^4),
\]

where $\theta_{eq} = 108.8^\circ$, $\theta_{ts} = 149.8^\circ$, and b is chosen to be 5.0 rad$^{-4}$.

The comparison of the scaled (with a scaling factor 0.95) ab initio and the fitted frequencies is given in Table 2. It is noted that an accurate fitting is not crucial here since the full-dimensional force field is only used in a qualitative mode-selective study.
3. The Semiclassical Method

The semiclassical method for computing tunneling splitting has been described previously [9, 13]. The new feature here is that a different Weutzel-Kramers-Brillouin (WKB) expression for level splitting in a 1-D potential is used. This more complicated form is valid for the entire range of energies and reduces to the one used previously for low energies. It is of the form [20]

\[
\Delta E = 4\hbar v \frac{\left( e^{-2S_c/v} + 1 \right)^{1/2} - 1}{\sqrt{\left( e^{-2S_c/v} + 1 \right)^{1/2} + 1}},
\]

(10)

where \( v \) is the frequency of the oscillator at energy \( E \) and \( S_c \) is the classical action integral.
\[ S_c = \int_{s_c}^{s_e} \sqrt{2m[V(s)-E]} \, ds. \] (11)

Using this WKB expression for a 1-D potential, the splitting for a multidimensional system can be approximated by [9, 13]

\[ \Delta E = 2\hbar \frac{d}{dt} \langle A(t) \rangle, \] (12)

with \( A(t) \) accumulated by propagating a classical trajectory

\[ A(t) = 2 \Sigma h(t-t_n) \sqrt{\left( e^{-2s_n/h} + 1 \right)^{1/2} - 1 \frac{1}{\left( e^{-2s_n/h} + 1 \right)^{1/2} + 1}}. \] (13)

Here, \( h(t-t_n) \) is the usual step function and \( t_n \) are the times that a trajectory is at the turning points. The brackets in equation (12) imply an average over an ensemble of trajectories with the same quantum number but different vibrational phases.

The key issue is the evaluation of the action integral \( S_c \). It was found in previous studies [4, 5] that the only mode strongly coupled to the reaction coordinate in the barrier region is the N–H stretch—the effect of which results in a reduction of the effective barrier height by about 1 kcal/mol. Considering the uncertainty in the ab initio calculation of the barrier height and width, it is reasonable to neglect the intramolecular couplings and just use the potential along the reaction coordinate \( V(\phi) \) [given by equation (4)] to compute the action integral. It is noted that the turning points are still determined in the full-dimensional space by propagating trajectories. The 1-D potential is used only in evaluating the action integral.

The mode-selective results described in the next section show that excitation of the reaction mode gives the dominant contribution to tunneling. Thus, in computing the thermal rate, it is
assumed that all the modes except the tunneling coordinate remain in their ground states and the thermal rate is approximated by

\[ k(T) = \frac{\sum_n k_n \exp \left( -\frac{\varepsilon_n}{k_B T} \right)}{\sum_n \exp \left( -\frac{\varepsilon_n}{k_B T} \right)}, \]  

(14)

with \( \varepsilon_n \) being the energy level in the 1-D potential \( V(\phi) \). The reaction rate \( k_n \) is given by

\[ k_n = v_n \]  

(15)

for \( \varepsilon_n > V_0 \), and

\[ k_n = \frac{\Gamma_n}{\hbar} = \frac{(\Delta E_n)^2}{4\hbar^2 v_n} \]  

(16)

for \( \varepsilon_n < V_0 \). Here, \( v_n \) is the oscillating frequency at energy \( \varepsilon_n \), \( V_0 \) is the barrier height of \( V(\phi) \), \( \Gamma_n \) is the level width, and \( \Delta E_n \) is the level splitting. The last equation can be seen from the WKB expressions for the level width and splitting at low energies

\[ \Gamma = \hbar v \exp \left( -\frac{2S_c}{\hbar} \right) \]  

(17)

and

\[ \Delta E = 2\hbar v \exp \left( -\frac{S_c}{\hbar} \right). \]  

(18)

4. Results and Discussion

Mode-selective effects in aziridine were investigated first using the full-dimensional potential. The calculations were carried out for initial conditions with 5 kcal/mol of energy
assigned to each normal mode above the zero-point level. The results show that excitation of the reaction coordinate mode has the dominant effect on tunneling, with the splitting being at least three orders of magnitude larger than that for excitation of any other mode. This provides some insight into the reaction mechanism and the observed non-RRKM behavior. The mode-selective results indicate that the intramolecular couplings may be weak enough that the rate of IVR is the slower and, hence, rate-limiting step. Thus, the observed reaction rates are independent of pressure, and, since excitations of many of the modes have no contributions to the state counting, the observed rates at high pressures deviate from those of RRKM predictions (see Figure 6 of Borchardt and Bauer [1]).

Based on the mode-selective results and the fact that the couplings between the reaction coordinate and the rest of the modes are not strong enough to significantly affect the effective barrier, it is reasonable to expect, as suggested previously [4, 5], that a 1-D treatment is adequate. The thermal rate is thus computed using equation (14) for the 1-D potential along the reaction coordinate, \( V(\phi) \). From equations (15) and (16), it is clear that one needs to obtain the oscillating frequency \( v_n \) and the level-splitting \( \Delta E_n \) for all the states contributing to the thermal rate. The frequency \( v_n \) was computed by first using adiabatic switching to confine the trajectories to the semiclassical eigen state and then propagating them one cycle to determine the period. The level-splitting was obtained from equation (10) by using the adiabatically switched trajectories to compute the action.

It is important to examine the accuracy of the semiclassical WKB formula equation (10). Table 3 shows comparisons of the semiclassical and exact quantum-mechanical level splittings for both the normal and deuterated species. The semiclassical splittings were computed by using equation (10), and the quantum ones were obtained by standard diagonalization of the Hamiltonian. The semiclassical and quantum results agree to within a few percent, demonstrating the accuracy of the WKB expression. (The quantum splittings for the first three deuterated states are missing because the accuracy of the calculation is not high enough.)
Table 3. Quantum Mechanical and Semiclassical Tunneling Splittings.

<table>
<thead>
<tr>
<th>n</th>
<th>Hydrogen Quantum Mechanical (kcal/mol)</th>
<th>Semiclassical (kcal/mol)</th>
<th>Deuterium Quantum Mechanical (kcal/mol)</th>
<th>Semiclassical (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.429 × 10^{-12}</td>
<td>0.458 × 10^{-12}</td>
<td>—</td>
<td>0.682 × 10^{-18}</td>
</tr>
<tr>
<td>1</td>
<td>0.166 × 10^{-9}</td>
<td>0.162 × 10^{-9}</td>
<td>—</td>
<td>0.354 × 10^{-15}</td>
</tr>
<tr>
<td>2</td>
<td>0.252 × 10^{-7}</td>
<td>0.248 × 10^{-7}</td>
<td>—</td>
<td>0.828 × 10^{-13}</td>
</tr>
<tr>
<td>3</td>
<td>0.223 × 10^{-5}</td>
<td>0.220 × 10^{-5}</td>
<td>0.120 × 10^{-10}</td>
<td>0.118 × 10^{-10}</td>
</tr>
<tr>
<td>4</td>
<td>0.125 × 10^{-3}</td>
<td>0.125 × 10^{-3}</td>
<td>0.116 × 10^{-8}</td>
<td>0.115 × 10^{-8}</td>
</tr>
<tr>
<td>5</td>
<td>0.450 × 10^{-2}</td>
<td>0.449 × 10^{-2}</td>
<td>0.816 × 10^{-7}</td>
<td>0.804 × 10^{-7}</td>
</tr>
<tr>
<td>6</td>
<td>0.924 × 10^{-1}</td>
<td>0.953 × 10^{-1}</td>
<td>0.420 × 10^{-5}</td>
<td>0.415 × 10^{-5}</td>
</tr>
<tr>
<td>7</td>
<td>—</td>
<td>—</td>
<td>0.159 × 10^{-3}</td>
<td>0.156 × 10^{-3}</td>
</tr>
<tr>
<td>8</td>
<td>—</td>
<td>—</td>
<td>0.425 × 10^{-2}</td>
<td>0.424 × 10^{-2}</td>
</tr>
<tr>
<td>9</td>
<td>—</td>
<td>—</td>
<td>0.707 × 10^{-1}</td>
<td>0.731 × 10^{-1}</td>
</tr>
</tbody>
</table>

Figure 2 provides a comparison of the calculated and experimental thermal-rate constants for both the normal and deuterated species. The barrier height was adjusted to 19.2 kcal/mol to fit the experimental result for hydrogen. This leads to good agreement for deuterium. The adjusted barrier height is close to the ab initio value of 18.2 kcal/mol, indicating that the intramolecular couplings do not significantly contribute to the effective barrier.

To illustrate the contributions from both classical and tunneling regimes, the contributions to the thermal rate of each individual state, \( k_n \exp \left(-\frac{\varepsilon_n}{k_B T}\right) \), are plotted in Figure 3. The two curves correspond to \( T = 300 \) and \( 360 \) K, which are near the low and high ends of the experimental data shown in Figure 2. The barrier height is slightly below \( \varepsilon_7 \). It is clear that, for the temperature range of the experiments, the major contributions to the rate are from the three states near the barrier: one below (\( n = 6 \)) and two above (\( n = 7, 8 \)). Thus, tunneling contributes about 1/3 of the total rate. Table 4 provides the quantitative results on the tunneling correction factor as a function of temperature defined as

\[
\kappa = \frac{k(T)_{\text{total}}}{k(T)_{\text{classical}}}.
\]  

(19)
Figure 2. The Thermal Rates as a Function of Temperature for Both the Normal and Deuterated Species. The Points and Lines Represent Experimental and Calculated Results, Respectively. The Experimental Data Are Taken From [2].

Figure 3. The Contribution to the Thermal Rate From Each Individual State, $k_n \exp\left(-\varepsilon_n/k_BT\right)$. The Barrier Is Slightly Below $\epsilon_7$.

The values for both the normal and deuterated species are given. The results obtained by using the Wigner formula [21]

$$\kappa_{\text{Wigner}} = 1 + \frac{1}{24} \left| \frac{\hbar \omega_{\text{barrier}}}{kT} \right|^2$$  \hspace{1cm} (20)
Table 4. Tunneling Correction Factors Calculated by Using the 1-D Potential V (φ).
The Results Are From the Exact Calculation Employing Equation (19)
and by Using the Wigner Formula Equation (20)

<table>
<thead>
<tr>
<th>T</th>
<th>Hydrogen</th>
<th></th>
<th>Deuterium</th>
<th></th>
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<tbody>
<tr>
<td></td>
<td>κ</td>
<td>κWigner</td>
<td>κ</td>
<td>κWigner</td>
</tr>
<tr>
<td>260</td>
<td>1.88</td>
<td>1.79</td>
<td>1.32</td>
<td>1.40</td>
</tr>
<tr>
<td>280</td>
<td>1.66</td>
<td>1.68</td>
<td>1.26</td>
<td>1.34</td>
</tr>
<tr>
<td>300</td>
<td>1.52</td>
<td>1.59</td>
<td>1.22</td>
<td>1.30</td>
</tr>
<tr>
<td>320</td>
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<td>340</td>
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<td>360</td>
<td>1.30</td>
<td>1.41</td>
<td>1.15</td>
<td>1.21</td>
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<tr>
<td>380</td>
<td>1.25</td>
<td>1.37</td>
<td>1.13</td>
<td>1.18</td>
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<td>1.22</td>
<td>1.33</td>
<td>1.12</td>
<td>1.17</td>
</tr>
</tbody>
</table>

are also given for comparison. It is seen that the Wigner formula works well, despite the fact that it is derived for the single barrier (no well) case, while this case is a double-well system.

At low energies where the energy levels are widely separated, the system should exhibit periodic oscillations between the wells, with the oscillating frequency proportional to the tunneling splitting, which can be measured spectroscopically. At high energies where the density of states is high and the intramolecular couplings are strong, tunneling becomes a rate process when the level broadening exceeds the splitting. These calculations provide an explanation for experimental observation of rate processes rather than level splittings [1, 2]; the splittings of the low-lying states are too small to be measured; the contribution to the thermal rates comes mainly from the states near the barrier top, where the anharmonicity is large and the density of states is high due to the large number of degrees of freedom of the molecule; hence, reaction rates, rather than splittings, were observed.

5. Conclusions

The intramolecular conversion in aziridine has been investigated. Ab initio calculations at the MP2 level have been performed, and the results have been used to construct a potential
energy surface that includes all 18 vibrational degrees of freedom. This full-dimensional potential was used to study the mode-selective effects by employing the multidimensional semiclassical approach [13], and it was found that excitations of modes other than the reaction mode make negligible contributions to the thermal rate. Thus, the previous conclusion [4, 5] is verified directly, that is, the problem of computing thermal rates can be reduced to a simple 1-D case.

This study provides some explanations for the experimental findings [1, 2]. The mode-selective results indicate that the intramolecular couplings may be weak, and, thus, the slow IVR is the rate-limiting step, leading to the pressure-independent reaction rates. Moreover, the observed rates at high pressures deviate from those of RRKM calculations [1] because many of the modes make no significant contributions. The results also show that the level splittings of the low energy states are too small to be observed, and, in the experimental temperature range, the states near the barrier top dominate the rate. These are consistent with the results of Rom, Ryaboy, and Moiseyev [4]. Thus, rate processes rather than splittings were observed due to large anharmonicity and high density of states near the barrier top.
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6. References


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A Semiclassical Study of Tunneling Effects in Aziridine

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The tunneling effects in the molecular inversion of aziridine are investigated. A full-dimensional potential was constructed based on ab initio results and used to study the effect of vibrational excitations on tunneling. Using the semiclassical approach that incorporates tunneling into classical trajectory calculations, it is found that excitations of all the modes except the reaction coordinate have negligible effects on tunneling. This allows accurate thermal-rate calculations carried out by using a one-dimensional (1-D) model. (This is in accord with the conclusions of the work by N. Rom, V. Ryaboy, and N. Moiseyev [Chemical Physics Letters, vol. 204, p. 175, 1993] and by Z. Smedarchina, W. Siebrand, and M. Z. Zgierski [Journal of Chemical Physics, vol. 102, p. 7024, 1995].) A 1-D Wurtz-Kramers-Brillouin (WKB) formula was employed to obtain the level splitting and was found to be very accurate based on comparisons with the quantum results. Furthermore, the calculated thermal rates are in good agreement with the experimentally measured values. The results provide insight into the reaction mechanism and explanations for the experimental findings of non-Rice-Ramsperger-Kassel-Marcus (RRKM) behavior and incoherent tunneling.
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