

# Modeling proton mobility in acidic zeolite clusters. II. Room temperature tunneling effects from semiclassical rate theory

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We have developed a novel semiclassical transition state theory (SC-TST) for truncated parabolic barriers, based on the formulation of Hernandez and Miller [Chem. Phys. Lett. **214**, 129 (1993)]. Our SC-TST rate coefficient has the form  $k^{\text{SC-TST}} = k^{\text{TST}} \cdot \Gamma$ , where  $\Gamma$  depends on the zero point corrected barrier,  $\Delta E_0$ , and the barrier curvature,  $|\omega_F^\ddagger|$ . Our rate expression is stable to arbitrarily low temperatures, as opposed to purely harmonic SC-TST, because we identify the maximum possible semiclassical action in the reaction coordinate. For low temperatures, we derive an analytical approximation for  $\Gamma$  that is proportional to  $e^{\beta \Delta E_0}$ . We develop a theory for the tunneling crossover temperature,  $T_x$ , yielding  $k_B T_x \cong \hbar |\omega_F^\ddagger| \Delta E_0 / (2\pi \Delta E_0 - \hbar |\omega_F^\ddagger| \ln 2)$ , which generalizes the harmonic theory for systems with large but finite barriers. We have calculated rate coefficients and crossover temperatures for the O(1)→O(4) jump in H–Y and D–Y zeolites, yielding  $T_x = 368$  K and 264 K, respectively. These results suggest that tunneling dominates proton transfer in H–Y up to and slightly above room temperature, and that true proton transfer barriers are being underestimated by neglecting tunneling in the interpretation of experimental mobility data.

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## I. INTRODUCTION

Zeolites are nanoporous, shape-selective catalysts widely used in the chemical industry for applications ranging from petroleum cracking to fine chemical synthesis.<sup>1</sup> Many reactions make use of the acidic properties of zeolites; most of these involve proton transfer reactions as elementary steps. To begin developing a microscopic picture for zeolite catalysis, it is crucial to model the dynamics of these proton transfer events.<sup>2</sup> The potentially quantum mechanical nature of proton transfer necessitates a reaction rate theory that accounts for quantum effects, while remaining sufficiently tractable for the complexity of problems found in zeolite science.<sup>2–4</sup> In this article, we develop a novel semiclassical transition state theory and apply it to the calculation of quantum rate coefficients for the O(1)→O(4) proton transfer in H–Y zeolite.

Several sophisticated quantum rate theories are presently available, based either on flux correlation functions,<sup>5,6</sup> transition state theory,<sup>7–12</sup> or instanton theory.<sup>4,13</sup> To apply a quantum rate theory to a many-body reactive system such as a zeolite cluster model, the theory should require a realistically limited set of potential energy parameters, because of the significant expense of *ab initio* calculations used to obtain those parameters. The simplest such theory is harmonic semiclassical transition state theory (SC-TST),<sup>14,15</sup> which only requires energies and frequencies at the reactant minimum and transition state. Unfortunately, this theory only ap-

plies when quantum effects are small, diverging at  $T = \hbar |\omega_F^\ddagger| / 2\pi k_B$  where  $|\omega_F^\ddagger|$  is controlled by the curvature of the barrier. Hernandez and Miller have reported a non-separable SC-TST that remains stable, and accounts for barrier anharmonicity and reaction path curvature.<sup>8</sup> However, for many complex problems of chemical and materials science interest, the cubic and quartic force constants required to parametrize their theory<sup>16</sup> are impractical to obtain from electronic structure calculations. In a similar way, the extended potential energy information required by the instanton method<sup>4</sup> may also be difficult to obtain for very complex systems.

We believe that harmonic SC-TST can provide a useful and reliable starting point for computational materials science, because energy second derivatives are available for a wide variety of electronic structure methods. Moreover, a partial cancellation of error is expected from a harmonic theory because barrier anharmonicity tends to decrease tunneling probabilities, while corner-cutting tends to increase them. The instability of harmonic SC-TST arises from assuming that the barrier remains parabolic *ad infinitum*. In the present article, we develop a *stable* harmonic SC-TST by re-introducing the ground state of reactants, which is reminiscent of the truncated parabolic barrier considered by Bell in 1934.<sup>17</sup> While the theory developed by Bell is only accurate in the deep tunneling regime, and the purely harmonic SC-TST is valid only at elevated temperatures where tunneling corrections are small, our approach smoothly connects the low and high temperature limits, as discussed below. We thus arrive at a quantum rate theory that is easy to param-

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etize and evaluate, remains stable to arbitrarily low temperatures, and is amenable to an analytical solution in certain limits. In a forthcoming publication, we will quantify the accuracy of this approach by comparing with quantum flux correlation calculations on model gas phase and condensed phase systems.<sup>18</sup>

Using our stabilized harmonic SC-TST, we explore the importance of tunneling for proton transfer in H–Y zeolite. We find it convenient to express our results in terms of the tunneling crossover temperature,  $T_x$ , below which tunneling becomes dominant and above which tunneling becomes negligible. We develop an analytical theory for  $T_x$  that depends upon the zero point vibrational energy corrected barrier height,  $\Delta E_0$ , as well as  $|\omega_F^\ddagger|$ . Consistent with our intuition from elementary quantum theory, we find that  $T_x$  is much more sensitive to changes in  $|\omega_F^\ddagger|$  than it is to changes in  $\Delta E_0$ . Using parameters from high level electronic structure calculations on zeolite cluster models, calculated in the previous paper, denoted Paper I, we find that tunneling dominates proton transfer in H–Y up to and slightly above room temperature, and that true proton transfer barriers are being underestimated by neglecting tunneling in the interpretation of experimental mobility data.<sup>19–21</sup>

The remainder of this paper is organized as follows: in Sec. II A we review previous versions of SC-TST, in Sec. II B we describe our stabilized harmonic SC-TST, and in Sec. II C we derive the high and low temperature limits of our new formula. In Sec. III A we discuss the results of our proton transfer calculations for H–Y and D–Y in the context of tunneling crossover temperatures, and in Sec. III B we describe the consequences for experimental mobilities in zeolites. In Sec. IV we give concluding remarks and speculate on areas for future study.

## II. RATE THEORY

The quantum rate theory developed below involves a modification and simplification of the elegant treatment given by Hernandez and Miller in 1993.<sup>8</sup> For completeness, we begin with the rate expression developed by Miller in 1975 for an  $F$ -dimensional system at temperature  $T$ , given by<sup>13</sup>

$$k(T) = \frac{1}{hQ^r} \int_{E_0}^{\infty} dE e^{-\beta E} N(E), \quad (2.1)$$

where  $Q^r$  is the total partition function of the reactant(s),  $E$  is the total energy,  $E_0$  is the ground state energy of the reactant(s),  $\beta = (k_B T)^{-1}$ ,  $k_B$  is Boltzmann's constant, and  $h = 2\pi\hbar$  is Planck's constant.  $N(E)$  is the cumulative reaction probability (CRP),<sup>13</sup> discussed below. Equation (2.1) is exact for gas phase reaction dynamics provided one accurately calculates the CRP.<sup>22</sup> Although the CRP was originally defined in the context of gas phase reactive scattering,<sup>13</sup> its calculation has since been pursued in condensed matter problems as well.<sup>23,24</sup> The gas phase CRP is defined by summing the state-to-state reaction probabilities over all energetically allowed reactant and product states at energy  $E$ , according to

$$N(E) = \sum_{n_r} \sum_{n_p} P_{n_p \leftarrow n_r}(E), \quad (2.2)$$

$$= \sum_{n_r} P_{n_r}(E). \quad (2.3)$$

In Eq. (2.3), the CRP is written in terms of initial-state-selected reaction probabilities,<sup>25</sup>  $P_{n_r}(E)$ , which provide a measure of the net flux through a surface spanning the product channel.<sup>25–27</sup> In the limit where all open reactant channels have initial-state-selected reaction probabilities that are either zero or one, the CRP becomes the *number* of reactant states that lead to products.

### A. Transition state theory

The standard *ansatz* in transition state theory (TST) is to replace the dynamically converged, net reactive flux from reactants to products with the instantaneous flux through the transition state dividing surface. TST is inspired by the fact that, although  $N(E)$  and  $k(T)$  are rigorously independent of the surface through which fluxes are computed,<sup>25</sup> the duration of dynamics required to converge the net reactive flux is usually shortest when using the transition state dividing surface. The TST approximation can be formulated for gas phase or condensed phase systems,<sup>28,29</sup> using classical or quantum mechanics.<sup>11</sup>

In what follows, we develop a uniformly stable, gas phase version of harmonic semiclassical TST, which is expected to give qualitatively reliable results when the tunneling dynamics are nearly separable. We apply the new theory below to a condensed phase system—proton transfer in zeolites—by focusing exclusively on flux through the proton transfer dividing surface. The approach is expected to give qualitatively reliable results for condensed phase systems, when the density of reaction-coordinate vibrational states is high for energies near the transition state energy. In a forthcoming publication we will quantify the accuracy of this approach by comparing with quantum flux correlation calculations on model gas phase and condensed phase systems.<sup>18</sup>

We formulate the TST approximation to the CRP in terms of transition state normal mode coordinates,  $(q_1, q_2, \dots, q_F)$ , where  $q_F$  is the reaction coordinate. The CRP is then approximated by<sup>30</sup>

$$N(E) \cong \sum_{n^\ddagger} P_{n^\ddagger}(E), \quad (2.4)$$

where  $n^\ddagger$  describes the vibrational quantum state of the  $F - 1$  stable modes at the saddle point. When  $P_{n^\ddagger}(E)$  is calculated semiclassically in the separable approximation, Eq. (2.4) becomes<sup>7,31</sup>

$$N(E) \cong \sum_{n^\ddagger} [1 + e^{2\theta(E, n^\ddagger)}]^{-1}, \quad (2.5)$$

where  $\theta$  is the barrier penetration integral for the reaction coordinate with reduced mass  $m$ . The challenge in semiclassical tunneling theory is creating a mapping from the multi-dimensional potential surface to the one-dimensional tunneling path required by the barrier penetration integral (*vide infra*).<sup>4</sup> This becomes particularly simple within the sepa-

rable approximation, because the total energy is given by  $E = E_F + \varepsilon_{n^\ddagger}$ , where  $\varepsilon_{n^\ddagger}$  is the conserved vibrational energy of the  $F-1$  stable modes, and  $E_F$  is the energy in the reaction coordinate obtained as the eigenvalue of  $\hat{H}_F = \hat{p}_F^2/2m + \hat{V}(q_F)$ . In terms of these quantities,  $\theta(E, n^\ddagger)$  is given by<sup>32</sup>

$$\theta(E, n^\ddagger) = \frac{1}{\hbar} \int_{x_1}^{x_2} dq_F \sqrt{2m[V(q_F) - (E - \varepsilon_{n^\ddagger})]}, \quad (2.6)$$

where the integration limits are the reaction coordinate turning points on the barrier, which satisfy the equation  $V(q_F) = E - \varepsilon_{n^\ddagger}$ , and become complex for reaction coordinate energies above the barrier. In general  $\theta(E, n^\ddagger)$  is real; positive for reaction coordinate energies below the barrier, and negative for energies above. Because the reaction coordinate energy has a minimum, ground state value, the barrier penetration integral has a maximum positive value for short range barriers.

To model corner-cutting dynamics arising from reaction path curvature, Hernandez, Miller, and co-workers extended the formulation in Eq. (2.5) to nonseparable multidimensional systems, by conceiving of  $\theta$  as a generalized barrier penetration integral.<sup>7,16</sup> Although the present article we focus on locally separable dynamics, we briefly review the 1993 nonseparable formulation of Hernandez and Miller<sup>8</sup> to put our method in perspective. The key insight<sup>7</sup> of the nonseparable theory is that Eq. (2.5) can still be used when dynamics are *integrable*, even when separability breaks down. Based on this idea, Hernandez and Miller expressed the energy near the transition state as

$$E \cong V^\ddagger + \sum_{i=1}^F \hbar \omega_i^\ddagger \left( n_i^\ddagger + \frac{1}{2} \right) + \sum_{i,j=1}^F x_{ij}^\ddagger \left( n_i^\ddagger + \frac{1}{2} \right) \left( n_j^\ddagger + \frac{1}{2} \right), \quad (2.7)$$

where  $V^\ddagger$  is the transition state potential energy, and  $\{\omega_i^\ddagger\}_{i=1, \dots, F-1}$  and  $\{x_{ij}^\ddagger\}_{i,j=1, \dots, F-1}$  are the real harmonic frequencies and anharmonic constants, respectively, of the  $F-1$  stable modes at the transition state. In Eq. (2.7),  $\omega_F^\ddagger$  is the imaginary frequency associated with the curvature at the top of the barrier,  $x_{FF}^\ddagger$  is a real anharmonic constant describing the anharmonicity of the barrier, and  $\{x_{iF}^\ddagger\}_{i=1, \dots, F-1}$  are imaginary anharmonicities determined by the reaction path curvature. For the  $F-1$  stable modes,  $\{\hbar(n_i^\ddagger + \frac{1}{2})\}$  are locally conserved semiclassical actions given by positive half-integer multiples of  $\hbar$ . For the reaction coordinate,  $\hbar(n_F^\ddagger + \frac{1}{2})$  is the locally conserved semiclassical action associated with the generalized barrier penetration integral according to<sup>7</sup>

$$\theta = -i\pi \left( n_F^\ddagger + \frac{1}{2} \right). \quad (2.8)$$

As with the separable case,  $\theta$  in Eq. (2.8) is real, and decreases with increasing energy. Equation (2.7) provides the energy as a quadratic function of  $\theta$  and  $n^\ddagger$ , which is inverted to obtain  $\theta(E, n^\ddagger)$  for use in Eq. (2.5).

## B. Stabilized harmonic semiclassical TST

The Hernandez and Miller nonseparable formulation is elegant in its treatment of barrier anharmonicity and reaction path curvature. Unfortunately, for many complex problems

of chemical and materials science interest, the cubic and quartic force constants that are required<sup>16</sup> to calculate the anharmonicities in Eq. (2.7) are impractical to obtain from electronic structure calculations. In a similar way, the extended potential energy information required by the instanton method<sup>4</sup> may also be difficult to obtain for very complex systems. As stated in the Introduction, we believe that harmonic semiclassical TST provides a useful and reliable starting point for computational materials science, because energy second derivatives are available for a wide variety of electronic structure methods. Moreover, partial cancellation of error is expected from a harmonic theory because barrier anharmonicity tends to decrease tunneling probabilities, while corner-cutting tends to increase them. Although the purely harmonic version of semiclassical transition state theory (SC-TST) has exhibited numerical instabilities and convergence problems in previous implementations,<sup>4,8</sup> we discuss below a stable expression for the rate coefficient that can be evaluated at all temperatures.

Pursuing the harmonic approximation, the energy in the region of the saddle point can be written as

$$E \cong V^\ddagger + \sum_{i=1}^{F-1} \hbar \omega_i^\ddagger \left( n_i^\ddagger + \frac{1}{2} \right) - \hbar |\omega_F^\ddagger| \theta / \pi. \quad (2.9)$$

Hernandez and Miller have shown that the integral over  $E$  in Eq. (2.1) can be transformed to an integral over  $\theta$ ,<sup>8</sup> giving

$$\begin{aligned} k^{\text{SC-TST}}(T) &= \frac{1}{hQ^r} \sum_{n^\ddagger} \int_{\theta_0}^{-\infty} d\theta \left( \frac{\partial E}{\partial \theta} \right) e^{-\beta E(\theta, n^\ddagger)} \frac{1}{1 + e^{2\theta}} \\ &= \frac{1}{hQ^r} \sum_{n^\ddagger} \left[ \frac{e^{-\beta E(\theta, n^\ddagger)}}{\beta(1 + e^{2\theta})} \right]_{-\infty}^{\theta_0} \\ &\quad + \frac{1}{\beta} \int_{-\infty}^{\theta_0} d\theta e^{-\beta E(\theta, n^\ddagger)} \frac{2e^{2\theta}}{(1 + e^{2\theta})^2}, \quad (2.10) \end{aligned}$$

where the second equality is obtained using integration by parts. Although integrating over energies is only strictly valid for gas phase systems, and hence is not rigorously correct for condensed matter systems such as zeolites, replacing discrete sums with integrals is consistent with semiclassical theory.<sup>33</sup>

Determining the correct value of  $\theta_0$  in Eq. (2.10), the transform of  $E_0$  in Eq. (2.1), is a crucial element of this theory and the major contribution in this paper. The Hernandez and Miller treatment resolved this issue by assuming that the integrand in Eq. (2.10) decays to zero well before  $\theta$  reaches its upper limit, effectively allowing the upper bound to be replaced with positive infinity. The surface term is then discounted for similar reasons. This often works because anharmonic effects introduce a factor of  $e^{-\beta x_{FF}^\ddagger \theta^2 / \pi^2}$  into the integrand, forcing a *rigorous* and faster decay to zero with increasing  $\theta$ . This is sufficient in many cases to reduce or eliminate errors involved with integrating to positive infinity. It has been noted that in the absence of these anharmonic effects there exists a temperature,  $T = \hbar |\omega_F^\ddagger| / 2\pi k_B$ , below which the integral in Eq. (2.10) will diverge because the integrand approaches infinity with increasing  $\theta$ .<sup>8</sup>

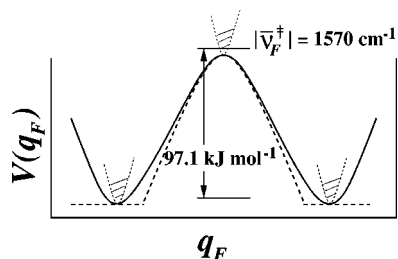


FIG. 1. Schematic of truncated parabolic barrier, showing orthogonal quantized modes.

It is especially at low temperatures when SC-TST needs to be applied. As such, it is imperative that a definition of  $\theta_0$  be determined that allows rate calculations at such temperatures. In the harmonic approximation, fortunately,  $\theta_0$  can be defined as the value of  $\theta$  that makes the energy in Eq. (2.9) equal to the lowest allowed energy, which is the zero point vibrational energy (ZPVE) corrected ground state of the reactant,  $E_0^r$ . The resulting value of  $\theta_0$  is then

$$\theta_0 = \frac{\pi \Delta E_0}{\hbar |\omega_F^\ddagger|}, \quad (2.11)$$

where  $\Delta E_0 = E_0^\ddagger - E_0^r$  is the ZPVE corrected classical barrier height. This choice is consistent with our separable approximation, because the largest amount of energy that can be removed from the molecule by descending the minimum energy pathway to reactants is exactly  $\Delta E_0$ , regardless of excitations in other modes. This value of  $\theta_0$  considerably simplifies the rate expression because it is strictly independent of  $n^\ddagger$ , thereby decoupling the summation and integration in Eq. (2.10).

Enforcing a finite upper limit to the integral in Eq. (2.10) within our harmonic theory is reminiscent of the truncated parabolic barrier considered by Bell in 1934,<sup>17</sup> shown schematically as the dashed line in Fig. 1. The theory developed by Bell is only accurate in the deep tunneling regime, while Eq. (2.10) smoothly connects the low and high temperature limits, as discussed in Sec. II C.

Using Eqs. (2.9) and (2.11) in Eq. (2.10), and removing all terms constant in  $\theta$  from the brackets, we arrive at our final expression for the SC-TST rate coefficient in the harmonic approximation:

$$\begin{aligned} k^{\text{SC-TST}}(T) &= \frac{k_B T}{h Q^r} \sum_{n^\ddagger} \exp \left\{ -\beta \left[ V^\ddagger + \sum_{i=1}^{F-1} \hbar \omega_i^\ddagger \left( n_i^\ddagger + \frac{1}{2} \right) \right] \right\} \\ &\times \left[ \frac{e^{\beta \Delta E_0}}{1 + e^{2\pi \Delta E_0 / \hbar |\omega_F^\ddagger|}} \right. \\ &\left. + \frac{1}{2} \int_{-\infty}^{\pi \Delta E_0 / \hbar |\omega_F^\ddagger|} d\theta e^{\beta \hbar |\omega_F^\ddagger| \theta / \pi} \text{sech}^2 \theta \right] \\ &= \frac{k_B T}{h} \cdot \frac{Q^\ddagger}{Q^r} \cdot \Gamma(T) = k^{\text{TST}}(T) \cdot \Gamma(T). \end{aligned} \quad (2.12)$$

The summation over  $n^\ddagger$  gives the total vibrational partition function at the transition state. The final result is identified as the transition state theory rate coefficient,  $k^{\text{TST}}(T)$ , multi-

plied by a tunneling correction factor,  $\Gamma(T)$ , which must be evaluated using a numerical integration scheme. Equation (2.12) is the main working formula in this paper. The only *ab initio* data required to calculate  $k^{\text{SC-TST}}(T)$  are the energies and harmonic vibrational frequencies at the two relevant stationary points: reactant minimum and transition state. In Paper I, we established convergence of these parameters with respect to basis set and level of theory, by focusing on small cluster models of H-Y. An approximate correction to the barrier accounting for long range interactions, which are ignored in our cluster models, is taken from the embedded cluster calculations reported by Sauer *et al.*,<sup>34</sup> and is used to predict our final barrier height. Those results will be utilized in rate calculations presented in Sec. III of the current work.

### C. High and low temperature limits of $\Gamma(T)$

To examine the plausibility of our new tunneling correction factor in Eq. (2.12), and to relate this factor to previous results, we consider the high and low temperature limits of  $\Gamma(T)$ . First we consider the high temperature limit, where  $\beta \rightarrow 0$ , in two cases: (i) where  $E_0^r \rightarrow -\infty$  so that  $\Delta E_0 \rightarrow \infty$ , i.e., the simple parabolic barrier; and (ii) where  $E_0^r$  and  $\Delta E_0$  remain finite, i.e., the truncated parabolic barrier. In the former case, the surface term vanishes if  $\beta \hbar |\omega_F^\ddagger| < 2\pi$ , and the integral becomes

$$\begin{aligned} \Gamma(T) &= \frac{1}{2} \int_{-\infty}^{\infty} d\theta e^{\beta \hbar |\omega_F^\ddagger| \theta / \pi} \text{sech}^2 \theta = \frac{\beta \hbar |\omega_F^\ddagger| / 2}{\sin(\beta \hbar |\omega_F^\ddagger| / 2)} \\ &= 1 + \frac{1}{24} \left( \frac{\beta \hbar |\omega_F^\ddagger|}{\pi} \right)^2 + \frac{7}{5,760} \left( \frac{\beta \hbar |\omega_F^\ddagger|}{\pi} \right)^4 \\ &\quad + \frac{31}{967,680} \left( \frac{\beta \hbar |\omega_F^\ddagger|}{\pi} \right)^6 + \dots, \end{aligned} \quad (2.13)$$

which is well known from the work of Wigner,<sup>14</sup> Bell,<sup>15</sup> and Hernandez and Miller.<sup>8</sup> In the truncated parabola case, the following expansion arises:

$$\begin{aligned} \Gamma(T) &= 1 + \sum_{n=1}^{\infty} \frac{1}{n!} \left( \frac{\beta \hbar |\omega_F^\ddagger|}{\pi} \right)^n \left[ \frac{\theta_0^n}{1 + e^{2\theta_0}} \right. \\ &\quad \left. + \frac{1}{2} \int_{-\infty}^{\theta_0} d\theta \theta^n \text{sech}^2 \theta \right], \end{aligned} \quad (2.14)$$

where  $\theta_0$  is given by Eq. (2.11). Although this expansion is formally different from that in Eq. (2.13), as evidenced by the odd powers of  $(\beta \hbar |\omega_F^\ddagger| / \pi)$  in Eq. (2.14), the two expansions are nearly identical up to the  $n=9$  term in Eq. (2.14) when using the high level electronic structure parameters calculated in Paper I. Conceptually, the  $n=0$  term represents classical mechanics at the top of the barrier, which is valid for high temperatures, while higher terms in the expansion represent tunneling dynamics at successively lower energies, which become important at lower temperatures. Using the parameters from Paper I, the  $n=9$  term is the first one that is sensitive to truncating the parabola, i.e., sensitive to the presence of the ground state of reactants.

In the low temperature limit, where  $\beta \rightarrow \infty$ , we can replace  $\text{sech}^2 \theta$  with  $4e^{-2\theta}$  in Eq. (2.12), since  $\beta \hbar |\omega_F^\ddagger| \gg 2\pi$ .

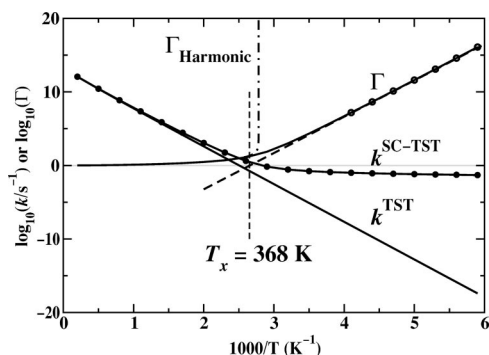


FIG. 2. Arrhenius plot of  $k^{\text{TST}}(T)$ ,  $\Gamma(T)$ , and  $k^{\text{SC-TST}}(T)$  high level electronic structure results for the asymmetric 3T cluster described in Paper I.

To simplify the final expression, we also assume that  $2\pi\Delta E_0/\hbar|\omega_F^\ddagger| \gg 1$ , which is valid for most systems exhibiting rare event dynamics. With these approximations, the tunneling correction factor becomes

$$\Gamma(T) \rightarrow \tilde{\Gamma}(T) = e^{\beta\Delta E_0} \cdot e^{-2\pi\Delta E_0/\hbar|\omega_F^\ddagger|} \left( 1 + \frac{2\pi}{\beta\hbar|\omega_F^\ddagger|} \right). \quad (2.15)$$

It is noteworthy that at low temperatures, our formula for  $\Gamma(T)$  becomes proportional to  $e^{\beta\Delta E_0}$ , hence eliminating the classical Arrhenius temperature dependence from  $k^{\text{TST}}(T)$ , as is well known from both experiment and theory. Thus, our tunneling correction factor, which derives its behavior from the upper bound to the integral in Eq. (2.12), clearly exhibits the correct low and high temperature limits, and hence provides a qualitatively reliable method for calculating quantum rate coefficients for nearly separable systems.

### III. RESULTS AND DISCUSSION

Armed with the energies and harmonic vibrational frequencies at the reactant minimum and transition state from Paper I, we use Eq. (2.12) to compute both the TST and SC-TST rate coefficients. The SC-TST calculation is stable at any temperature because of the upper bound on the integral in Eq. (2.12). Figure 2 shows an Arrhenius plot of these rate coefficients at temperatures from below 200 to above 1000 K, for the O(1) to O(4) proton jump in H–Y zeolite. We use the most accurate input parameters from Paper I to calculate  $\Gamma(T)$ , namely  $\Delta E_0 = 97.1 \text{ kJ mol}^{-1}$  and  $|\bar{\nu}_F^\ddagger| = |\omega_F^\ddagger|/2\pi c = 1570 \text{ cm}^{-1}$ .

#### A. Tunneling crossover temperatures

In the high temperature regime, Fig. 2 shows no difference between the SC-TST and the TST rate coefficients. At low temperatures, as tunneling becomes more important and classical barrier crossings become more rare, the SC-TST rate coefficient develops a very weak temperature dependence because of the factor of  $e^{\beta\Delta E_0}$  in  $\Gamma(T)$  [see Eq. (2.15)]. At intermediate temperatures the two approximately linear sections of this graph join smoothly. We define a tunneling crossover temperature,  $T_x$ , as the point where the two linear sections would hypothetically intersect; at temperatures below  $T_x$  tunneling is dominant and at temperatures

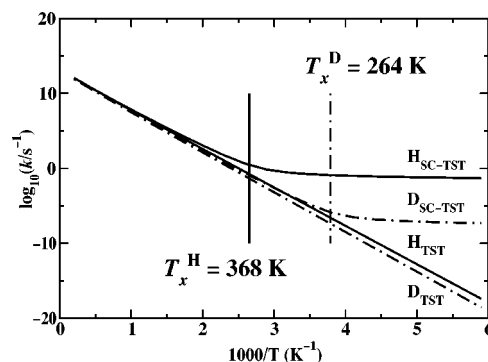


FIG. 3. Kinetic isotope effect of proton and deuteron transfer in zeolite Y. H–Y data shown as solid lines, D–Y data shown as dash–dotted lines.

above  $T_x$  tunneling becomes negligible.<sup>4</sup> It is clear that at  $T_x$ , the SC-TST rate coefficient is appreciably larger than the TST rate coefficient, possibly by more than an order of magnitude [e.g.,  $\Gamma(T_x) = 21.3$  in Fig. 2]. Thus,  $T_x$  is not a point at which a distinct change in mechanism occurs, but rather is a point along a continuous but rapid change, placing a boundary on the temperature regime of applicability of traditional transition state theory.

We prefer for numerical convenience to obtain  $T_x$  by analyzing  $\Gamma(T)$ . In particular, Fig. 2 shows that in both the high and low temperature limits,  $\log \Gamma(T)$  vs  $1/T$  is nearly a straight line. Consistent with our previous definition of  $T_x$ , we obtain  $T_x$  as the temperature where *these* two linear sections intersect. The high temperature limit of  $\Gamma(T)$  is 1, while the low temperature limit of  $\Gamma(T)$  is given in Eq. (2.15). As such, the temperature for which  $\tilde{\Gamma}(T) = 1$  is  $T_x$ . In practice, we calculate  $T_x$  as the root of the equation  $\ln \tilde{\Gamma}(T) = 0$ , using the bisection method.<sup>35</sup>

The crossover temperature obtained in this way from Fig. 2 is 368 K. It is worth noting the sensitivity of  $T_x$  to changes in both  $\Delta E_0$  and  $|\bar{\nu}_F^\ddagger|$  by their respective uncertainties, as determined in Paper I. Changing the barrier height by  $\pm 10 \text{ kJ mol}^{-1}$  alters the slope of the exponentially dependent portion of  $\Gamma(T)$ , but only changes  $T_x$  to 366 K (larger barrier) or 369 K (smaller barrier). Changing  $|\bar{\nu}_F^\ddagger|$  by  $\pm 200 \text{ cm}^{-1}$ , however, produces crossover temperatures of 415 K (larger  $|\bar{\nu}_F^\ddagger|$ ) or 319 K (smaller  $|\bar{\nu}_F^\ddagger|$ ). Thus, changes to the system that facilitate tunneling will raise  $T_x$ ; increasing  $|\omega_F^\ddagger|$  and, to a much lesser extent, decreasing  $\Delta E_0$  increases both  $T_x$  and the tunneling probability.

To estimate the kinetic isotope effect on jump rates in acidic zeolites, we recalculated all the harmonic frequencies for a cluster model of D–Y zeolite, giving  $\Delta E_0 = 100.7 \text{ kJ mol}^{-1}$  and  $|\bar{\nu}_F^\ddagger| = 1135 \text{ cm}^{-1}$ . As expected, the ZPVE corrected barrier increases because the ZPVE of the reaction coordinate in the reactant well is reduced upon isotopic substitution. Also as expected, the barrier frequency is reduced from the H–Y value by a factor of *ca.*  $1/\sqrt{2}$ . TST and SC-TST jump rate coefficients for H–Y and D–Y are compared in Fig. 3, showing clearly that at room temperature, tunneling is more important for proton transfer than it is for deuteron transfer. Indeed, the tunneling crossover temperature for D–Y obtained from Fig. 3 is 264 K, also re-

TABLE I. Absolute rate coefficients and tunneling correction factors for 3T clusters using high level electronic structure results.

$T(K)$	Symmetric 3T $R_{\text{Si-Si}}=5.8 \text{ \AA}$		Symmetric 3T $R_{\text{Si-Si}}=6.0 \text{ \AA}$		Asymmetric 3T $R_{\text{Si-Si}}=5.93-5.96 \text{ \AA}$		Best $\Delta E_0$ (see the text)	
	$k(T)(s^{-1})$	$\Gamma(T)$	$k(T)(s^{-1})$	$\Gamma(T)$	$k(T)(s^{-1})$	$\Gamma(T)$	$k(T)(s^{-1})$	$\Gamma(T)$
200	$3.45 \times 10^3$	$2.74 \times 10^7$	$3.16 \times 10^{-2}$	$4.31 \times 10^{13}$	2.56	$2.14 \times 10^{10}$	$6.46 \times 10^{-2}$	$4.04 \times 10^{11}$
300	$1.18 \times 10^4$	$2.67 \times 10^2$	$8.14 \times 10^{-2}$	$5.64 \times 10^4$	8.40	$1.83 \times 10^3$	$2.12 \times 10^{-1}$	$3.80 \times 10^3$
400	$1.81 \times 10^5$	6.90	1.22	$1.88 \times 10^1$	$2.45 \times 10^2$	8.56	9.15	8.71
500	$3.37 \times 10^6$	2.74	$1.51 \times 10^2$	3.68	$1.60 \times 10^4$	2.92	$1.14 \times 10^3$	2.93
600	$3.07 \times 10^7$	1.19	$6.85 \times 10^3$	2.24	$3.61 \times 10^5$	1.98	$3.98 \times 10^4$	1.98
	$\Delta E_0 = 62.8 \text{ kJ/mol}$ $ \bar{v}_F^\ddagger  = 1548 \text{ cm}^{-1}$ $T_x = 367 \text{ K}$		$\Delta E_0 = 105.9 \text{ kJ/mol}$ $ \bar{v}_F^\ddagger  = 1695 \text{ cm}^{-1}$ $T_x = 397 \text{ K}$		$\Delta E_0 = 86.1 \text{ kJ/mol}$ $ \bar{v}_F^\ddagger  = 1570 \text{ cm}^{-1}$ $T_x = 369 \text{ K}$		$\Delta E_0 = 97.1 \text{ kJ/mol}$ $ \bar{v}_F^\ddagger  = 1570 \text{ cm}^{-1}$ $T_x = 368 \text{ K}$	

duced from the H–Y value of 368 K by a factor of *ca.*  $1/\sqrt{2}$ .

It is interesting that variations in  $\Delta E_0$  and  $|\bar{v}_F^\ddagger|$  produce qualitatively different changes in  $T_x$ . The same qualitative sensitivity is exhibited by the simple rectangular barrier, where the logarithm of the tunneling probability depends linearly on the barrier width, but only depends on the square root of the barrier height.<sup>32</sup> An analysis of our low temperature tunneling correction factor,  $\tilde{\Gamma}(T)$  in Eq. (2.15), quantitatively accounts for the sensitivities found above for  $T_x$ . In particular, if we ignore the surface term in Eq. (2.12) when deriving  $\tilde{\Gamma}(T)$ , we arrive at Eq. (2.15), except with the last factor replaced by  $(2\pi/\beta\hbar|\omega_F^\ddagger|)$ . Using this simpler version of  $\tilde{\Gamma}(T)$  would give  $T_x = \hbar|\omega_F^\ddagger|/2\pi k_B = 360 \text{ K}$  for our system, precisely the temperature at which the purely harmonic theory diverges. The rapidly varying exponentials in Eq. (2.15) actually make  $T^* \equiv \hbar|\omega_F^\ddagger|/2\pi k_B$  a reasonable initial guess for  $T_x$ . If the slowly varying, third factor in Eq. (2.15) is evaluated at  $T = T^*$ , the equation  $\ln \tilde{\Gamma}(T) = 0$  can be solved analytically for  $T_x$ , yielding

$$T_x \cong \tilde{T}_x = \frac{\hbar|\omega_F^\ddagger|\Delta E_0/k_B}{2\pi\Delta E_0 - \hbar|\omega_F^\ddagger|\ln 2}. \quad (3.1)$$

Equation (3.1) deserves several remarks. First, our theory assumes that  $2\pi\Delta E_0 > \hbar|\omega_F^\ddagger|\ln 2$  to make  $T_x$  positive. Indeed, when  $2\pi\Delta E_0 \gg \hbar|\omega_F^\ddagger|\ln 2$ , the crossover temperature can be further approximated as

$$\tilde{T}_x \cong \frac{\hbar|\omega_F^\ddagger|}{2\pi k_B} \left( 1 + \frac{\hbar|\omega_F^\ddagger|\ln 2}{2\pi\Delta E_0} \right) = T^* \left( 1 + \frac{\ln 2}{2\theta_0} \right). \quad (3.2)$$

Using the high level parameters from Paper I, which give  $T^* = 360 \text{ K}$  and  $\theta_0 = 16.2$ , Eq. (3.2) predicts  $\tilde{T}_x = 368 \text{ K}$ , precisely that obtained from Fig. 2 and Eq. (2.15). As such, Eqs. (3.1) and (3.2) generalize the purely harmonic theory of  $T_x$  for systems with large but *finite* barriers. Second, the sensitivities of  $T_x$  to changes in  $\Delta E_0$  and  $|\omega_F^\ddagger|$  can now be estimated using Eqs. (3.1) and (3.2), giving

$$\begin{aligned} \frac{\partial(k_B\tilde{T}_x)}{\partial\Delta E_0} &= -\ln 2 \left( \frac{k_B\tilde{T}_x}{\Delta E_0} \right)^2 \cong - \left( \frac{\ln 2}{4\theta_0^2} \right) \\ \frac{\partial(k_B\tilde{T}_x)}{\partial(\hbar|\omega_F^\ddagger|)} &= +2\pi \left( \frac{k_B\tilde{T}_x}{\hbar|\omega_F^\ddagger|} \right)^2 \cong \frac{1}{2\pi}. \end{aligned} \quad (3.3)$$

Equations (3.3) indicate that  $\partial(k_B\tilde{T}_x)/\partial\Delta E_0$  is very small and uniformly negative, while  $\partial(k_B\tilde{T}_x)/\partial(\hbar|\omega_F^\ddagger|)$  is larger and uniformly positive, in complete qualitative and quantitative agreement with our findings above. Finally, it is interesting to note that, even if  $\hbar|\omega_F^\ddagger|$  were comparable to  $\Delta E_0$ ,  $\tilde{T}_x$  in Eq. (3.1) would still be much more sensitive to changes in  $\hbar|\omega_F^\ddagger|$  than it would be to changes in  $\Delta E_0$ , because of the factors of  $2\pi$  and  $\ln 2$ . Thus, these factors enforce the ubiquitous quantum mechanical rule that tunneling is controlled more by barrier width than it is by barrier height.

## B. Consequences for experimental mobilities in zeolites

In Paper I we modeled three different clusters with  $\text{H}_3\text{SiOAl}(\text{OH})_2\text{OSiH}_3^{-1}$  connectivity. Two clusters were constrained by enforcing a plane of symmetry along the SiO–AlOSi backbone, and by fixing the distance between the silicon atoms at two characteristic values: 5.8 Å and 6.0 Å. The third cluster was constructed from H–Y neutron diffraction data,<sup>36</sup> with fabricated SiH and OH bonds that were frozen in space. These clusters represent a sample of characteristic substrates for proton transfer in acidic zeolites, and illustrate how variations in local geometry affect the transfer rates.

Absolute rate coefficients and tunneling correction factors for proton transfer in our models of H–Y zeolite, as calculated using electronic structure data from Paper I, are tabulated in Table I, along with our best estimates of  $\Delta E_0$ ,  $|\bar{v}_F^\ddagger|$  and  $T_x$  for these clusters. The best available estimate for the barrier height is obtained by adjusting the classical barrier calculated by Sauer *et al.*,<sup>34</sup> which includes long range interactions, with our treatment of high level correlation effects and zero point vibrational energy differences, giving a value of  $\Delta E_0^{\text{Embed}}(\text{MP4}) \cong \Delta V_0^{\text{Embed}}(\text{B3LYP}) + [\Delta E_0^{3T}(\text{MP4}) - \Delta E_0^{3T}(\text{B3LYP})] + \Delta \text{ZPVE}^{3T}(\text{MP2}) = 100.9 + (86.1 - 76.3) - 13.6 \text{ kJ mol}^{-1} = 97.1 \text{ kJ mol}^{-1}$ . Using this value for  $\Delta E_0$  combined with our best vibrational analysis gives the results shown in the last column of Table I. We see that a higher barrier lowers the absolute rate coefficient by many orders of magnitude, but increases the value of  $\Gamma(T)$  by similar amounts at low temperatures. At high temperatures, the absolute rate coefficients exhibit the classical Arrhenius temperature dependence, while  $\Gamma(T)$  approaches its limiting

value of unity. The time scales obtained from these rate coefficients are long compared to typical time scales of molecular jumps in zeolites at ambient conditions,<sup>37</sup> suggesting that protons may appear static during the time it takes a molecule to sample the surface of a zeolite cage or channel. The crossover temperatures in Table I fall in the range 367–397 K.

It is interesting to note from Table I that as the Si–Si distance is varied, two competing effects emerge. Longer Si–Si distances produce larger barriers, which one might expect to cause a decrease in  $T_x$ . There is, however, a significant increase in  $|\bar{v}_F^\ddagger|$ , creating a barrier that is thinner near the transition state despite its increased height. Since tunneling probabilities are more sensitive to barrier width than they are to barrier height, the net effect turns out to be an *increase* in tunneling probabilities and also in  $T_x$  upon increasing the Si–Si distance. The overwhelming conclusion to be gleaned from these results is that, up to and even above room temperature, the dominant mechanism for proton mobility about an acid site is quantum mechanical tunneling through the potential barrier.

The conclusion that proton tunneling in zeolites is important at ambient conditions presents interesting consequences for the interpretation of proton mobilities measured near room temperature. In particular, assuming an Arrhenius temperature dependence for measured proton transfer rates in the tunneling regime will underestimate the true ZPVE corrected barrier. For example, Sarv *et al.*<sup>19</sup> reported proton transfer rates in H–Y zeolite at 298 K, 478 K, 568 K, and 658 K, a temperature range that we believe overlaps significantly with the tunneling regime. To explore the consequences of this, we computed rate coefficients at these temperatures using parameters from the last column in Table I, and forced an Arrhenius fit to these rate data, which in fact show clear non-Arrhenius temperature dependence, especially at 298 K. By this procedure we obtain an apparent activation energy of 60.3 kJ mol<sup>-1</sup>, which is in remarkably good agreement with the experimentally determined value of 61 kJ mol<sup>-1</sup>.<sup>19</sup> This level of agreement is likely to involve fortuitous cancellation of errors, considering the approximations we have made in the electronic structure and dynamics calculations. Nonetheless, this strongly suggests that true proton transfer barriers are being underestimated by neglecting tunneling when interpreting mobility data. On the other hand, our kinetic isotope studies of deuteron transfer in D–Y, which predict  $T_x=264$  K, suggest that Arrhenius fits of deuteron mobilities near room temperature should provide good estimates of deuteron transfer barriers.

#### IV. CONCLUDING REMARKS

We have developed a novel semiclassical transition state theory (SC-TST) for truncated parabolic barriers, based on the formulation of Hernandez and Miller.<sup>8</sup> Our SC-TST rate coefficient has the form  $k^{\text{SC-TST}}(T) = k^{\text{TST}}(T) \cdot \Gamma(T)$ , where  $k^{\text{TST}}(T)$  is the TST rate coefficient, and  $\Gamma(T)$  is the new tunneling correction factor, which is evaluated numerically.  $\Gamma(T)$  depends on temperature, the zero point vibrational energy (ZPVE) corrected barrier,  $\Delta E_0$ , and the curvature of the

barrier at the transition state,  $|\omega_F^\ddagger|$ . Our rate expression is easy to parametrize and evaluate, and is stable to arbitrarily low temperatures. Purely harmonic SC-TST, on the other hand, diverges at and below  $T = \hbar|\omega_F^\ddagger|/2\pi k_B$ . Our rate expression is stabilized at low temperatures by identifying the maximum possible semiclassical action in the reaction coordinate, associated with the ground state of the system.

We have analyzed the high and low temperature limiting forms of  $\Gamma(T)$ . For high temperatures, we derive an expansion for  $\Gamma(T)$  in powers of  $(\beta\hbar|\omega_F^\ddagger|/\pi)$ , which we relate to formulas reported by Wigner, Bell, and Hernandez and Miller. For low temperatures, we derive a simple, analytical approximation for  $\Gamma(T)$ , denoted  $\tilde{\Gamma}(T)$ , which is proportional to  $e^{\beta\Delta E_0}$  and thus eliminates the classical Arrhenius temperature dependence from  $k^{\text{TST}}(T)$ . We define a tunneling crossover temperature,  $T_x$ , as the temperature below which tunneling becomes dominant and above which tunneling becomes negligible. We evaluate  $T_x$  according to the equation  $\tilde{\Gamma}(T_x) = 1$ , which we solve approximately to yield  $k_B T_x \cong \hbar|\omega_F^\ddagger| \Delta E_0 / (2\pi \Delta E_0 - \hbar|\omega_F^\ddagger| \ln 2)$ . This formula generalizes the purely harmonic theory of  $T_x$  for systems with large but *finite* barriers.

Based on the high level electronic structure results reported in Paper I, we have calculated rate coefficients and crossover temperatures for the O(1) to O(4) jump in H–Y and D–Y zeolites. These rate coefficients suggest that protons may appear static on molecular diffusion time scales. Our best estimates of  $T_x$  are 368 K and 264 K for H–Y and D–Y, respectively, suggesting that quantum tunneling is the dominant mechanism for proton transfer in H–Y at and slightly above room temperature.

Forcing an Arrhenius fit to our H–Y rate coefficients calculated at the temperatures studied experimentally by Sarv *et al.*<sup>19</sup> ( $T = 298$ – $658$  K), yields an apparent activation energy of 60.3 kJ mol<sup>-1</sup> even though our input for  $\Delta E_0$  is 97.1 kJ mol<sup>-1</sup>. Because this apparent activation energy is in good agreement with the experimentally determined value of 61 kJ mol<sup>-1</sup>,<sup>19</sup> we believe that true proton transfer barriers are being underestimated by neglecting tunneling when interpreting mobility data. On the other hand, jump rates calculated for D–Y suggest that Arrhenius fits of deuteron mobilities near room temperature should provide good estimates of deuteron transfer barriers. In the future, experimental proton transfer rates on a wider range and finer mesh of temperatures, as well as more accurate theoretical calculations, will be required before the importance of proton tunneling in zeolites at ambient conditions is firmly established.

Our uniformly stable version of harmonic SC-TST described above is expected to give qualitatively reliable results when the tunneling dynamics are nearly separable. In a forthcoming publication, we will quantify the accuracy of this approach by comparing with quantum flux correlation calculations on model gas phase and condensed phase systems.<sup>18</sup> We will focus on tunneling dynamics at low temperatures, involving tunneling “paths” that are likely to access regions of configuration space where the local conservation of harmonic actions can seriously break down.

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