Analytical theory of benzene diffusion in Na-Y zeolite

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We have developed an analytical expression for the diffusion coefficient of benzene in Na-Y at infinite dilution in terms of fundamental rate coefficients, which has been confirmed by extensive kinetic Monte Carlo simulations. This model assumes that benzene jumps among S_{II} and W binding sites, located near Na^+ ions in 6-rings and in 12-ring windows, respectively. Our diffusion theory is based on $D=\frac{1}{6}ka^2$ where $a \cong 11$ Å is the intercage length and k is the cage-to-cage rate coefficient. We have determined that $k=k(S_{II}\to W)\cdot\frac{1}{2}\cdot 3[1+k(W\to W)/k(W\to S_{II})]$, a finding that has resolved discrepancies between theory and simulation and has suggested new interpretations of benzene diffusion in Na-Y. When $\alpha(T)\equiv k(W\to W)/k(W\to S_{II})$ is between 0 and 1, the factor $3[1+\alpha(T)]$ counts the number of thermally allowed target sites for cage-to-cage motion. Alternatively, when $\alpha(T)\gg 1$, benzene mobility is interpreted as interstitial diffusion, wherein k is controlled by the probability of W site occupancy multiplied by the rate of W→W jump processes. This limit is expected to arise with benzene loadings of four molecules per supercage. © *1997 American Institute of Physics.* [S0021-9606(97)50218-2]

I. INTRODUCTION

The transport properties of adsorbed molecules[1] play a central role in catalytic and separation processes[2] that take place within zeolite cavities.[3] Understanding the host–guest interactions that control molecular diffusion may suggest new materials with advanced performance. We have recently reported the results of analysis and simulation that greatly simplify our picture of benzene diffusion in Na–Y by focusing on the dynamics of cage-to-cage motion.[4,5] In this system benzene has two predominant binding sites.[6] In the primary site, denoted as S_{II}, benzene binds to Na^+ coordinated to a zeolite 6-ring; the secondary site, denoted as W, involves benzene in a 12-ring window separating two adjacent supercages (cf. Figs. 1 and 2). Although hops really take place among S_{II} and W sites, imagining that diffusion through Na-Y involves jumps from ''cage site'' to ''cage site'' reduces the problem to diffusion on a tetrahedral lattice, as shown in Fig. 3. In the case of random hopping on a tetrahedral lattice, we have rigorously proven that $D=\frac{1}{6}ka^2$ where $a\cong 11$ Å is the intercage length and $1/k$ is mean cage residence time.[4,5] This result is interesting because we obtain the simple-cubic result even though the simple-cubic partitioning of Na-Y is invalid at the cage-to-cage length scale.

In our previous study[5] k was equated to $\frac{1}{2}\cdot 4\cdot k(S_{II}\to W)$ where the factor of one half accounts for randomizing in the W site, and the factor of 4 accounts for the four ways to leave the supercage through one of the four windows. While this formula for k gives a rather straightforward picture for cage-to-cage kinetics, it also gives persistent, systematic error when compared with simulation over a broad range of system parameters, as discussed in Sec. III. Below we present an analytical treatment of this problem that resolves the discrepancies alluded to above, and also suggests new interpretations for benzene diffusion in Na-Y.

The remainder of this paper is organized as follows: in Sec. II we present our analysis of cage-to-cage motion including various limits and interpretations for k. In Sec. III we describe the simulation methodology used and results obtained for comparison with our analytical theory. In Sec. IV we conclude by speculating on the applicability of our approach for other host–guest systems.

II. ANALYSIS OF CAGE-TO-CAGE MOTION

A. General formulation

We begin our analysis of benzene cage-to-cage motion in Na-Y zeolite by imagining a trajectory executed by a single benzene molecule through Na-Y, hopping among S_{II} and W sites. In the limit of a *very* long trajectory, mean residence times at S_{II} and W sites can be used to calculate hopping rate coefficients and equilibrium coefficients in accord with the ergodic hypothesis.[7] The mean supercage residence time, $\langle\tau\rangle_{\text{cage}}$, is then given by

$$\langle\tau\rangle_{\text{cage}}=\frac{T}{N_{\text{cc}}}=\frac{1}{N_{\text{cc}}}(T_{S_{II}}+T_W)=\frac{T_W}{N_{\text{cc}}}\left(\frac{T_{S_{II}}}{T_W}+1\right)$$

$$\xrightarrow{T\to\infty}\frac{T_W}{N_{\text{cc}}}[K_{\text{eq}}(W\to S_{II})+1], \tag{2.1}$$

where $T=T_{S_{II}}+T_W$ is the total time of the trajectory, $T_{S_{II}}$ and T_W are the total residence times at S_{II} and W sites, respectively, and N_{cc} is the number of cage-to-cage jumps during the trajectory. The long time limit in Eq. (2.1) ensures convergence of $T_{S_{II}}/T_W$ to the equilibrium coefficient $K_{\text{eq}}(W\to S_{II})=2k(W\to S_{II})/k(S_{II}\to W)$, where $k(W\to S_{II})$ and $k(S_{II}\to W)$ are fundamental rate coefficients (cf. Figs. 1 and 2), and the factor of 2 arises because each W site is shared between two adjacent supercages. The long time limit allows T_W to be expressed as

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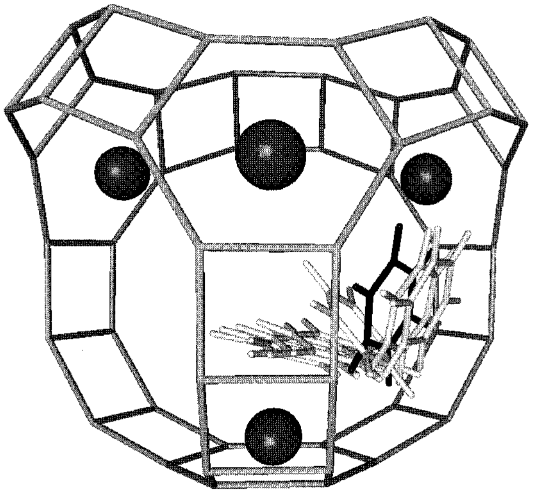

FIG. 1. $S_{II}\leftrightarrow W$ minimum energy path with transition state indicated in bold.

$$T_W = N_W \cdot \frac{T_W}{N_W} = N_W \cdot \langle \tau \rangle_W \overset{T\to\infty}{\to} \frac{N_W}{k_{\text{tot}}(W)}$$

$$= N_W \{6[k(\mathrm{W}\to \mathrm{S}_{II}) + k(\mathrm{W}\to \mathrm{W})]\}^{-1}, \tag{2.2}$$

where N_W is the number of visits to W sites, $\langle \tau \rangle_W$ is the mean W site residence time, $k_{\text{tot}}(W) = 1/\langle \tau \rangle_W$ is the total rate of leaving the W site, $k(\mathrm{W}\to\mathrm{W})$ is another fundamental rate coefficient, and the factor of 6 counts available target sites in the Na-Y supercage structure. The long trajectory limit allows one further simplification, namely that $N_{\text{cc}} = N_W/2$. The factor of $\frac{1}{2}$ accounts for randomizing in the W site which halves the probability to leave the cage.

Putting these results together, we have

$$\langle \tau \rangle_{\text{cage}} = \frac{K_{\text{eq}}(\mathrm{W}\to\mathrm{S}_{II}) + 1}{3[k(\mathrm{W}\to\mathrm{S}_{II}) + k(\mathrm{W}\to\mathrm{W})]}, \tag{2.3}$$

which represents an exact, analytical solution of the Master Equation determining cage-to-cage motion in terms of fundamental hopping rate coefficients. Before proceeding, we note that Eq. (2.3) contains all the fundamental rate coefficients in our system except for $k(\mathrm{S}_{II}\to\mathrm{S}_{II})$, which controls benzene intracage motion. As such, while diffusion measurements can probe many aspects of this system, they are insensitive to the dynamics of intracage motion.[4,5,8,9] (See Note added in proof and Ref. 10.)

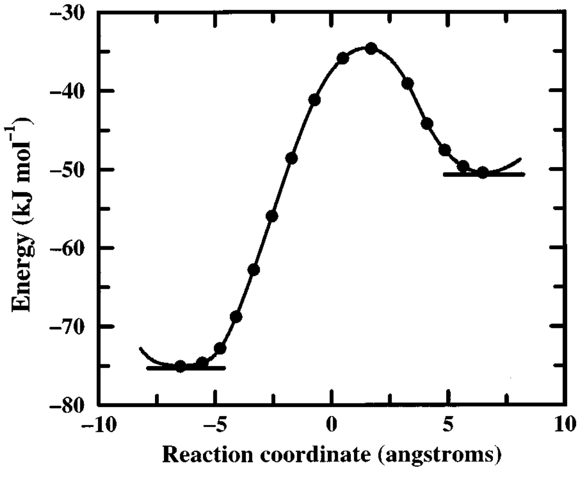

FIG. 2. $S_{II}\leftrightarrow W$ energetics with 41 kJ mol^{-1} activation energy.

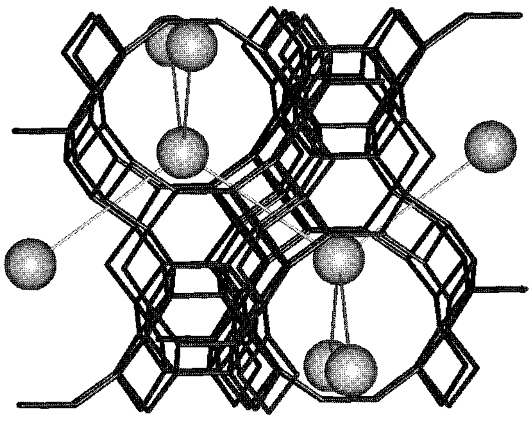

FIG. 3. Tetrahedral connectivity of supercages in the Na-Y unit cell. Balls represent supercage ''sites'' and sticks represent cage-to-cage jumps.

The remainder of this section is devoted to examining various limits of Eq. (2.3) and interpreting the results. In what follows we focus on the rate coefficient for cage-to-cage motion, $k = 1/\langle \tau \rangle_{\text{cage}}$.

B. $K_{\text{eq}}(\mathrm{W}\to\mathrm{S}_{II}) \gg 1$

Recently reported docking calculations[4,10] of benzene at the S_{II} and W sites in Na-Y suggest that the S_{II} site is more stable by ~25 kJ mol^{-1}, indicating that $K_{\text{eq}}(\mathrm{W}\to\mathrm{S}_{II}) \gg 1$ for most relevant temperatures. This allows us to express the intercage rate coefficient as

$$k = \frac{3[k(\mathrm{W}\to\mathrm{S}_{II}) + k(\mathrm{W}\to\mathrm{W})]}{K_{\text{eq}}(\mathrm{W}\to\mathrm{S}_{II})} \tag{2.4}$$

$$= \frac{3}{2} \cdot \frac{k(\mathrm{S}_{II}\to\mathrm{W})}{k(\mathrm{W}\to\mathrm{S}_{II})} \cdot [k(\mathrm{W}\to\mathrm{S}_{II}) + k(\mathrm{W}\to\mathrm{W})]$$

$$= k(\mathrm{S}_{II}\to\mathrm{W}) \cdot \frac{1}{2} \cdot 3\left[1 + \frac{k(\mathrm{W}\to\mathrm{W})}{k(\mathrm{W}\to\mathrm{S}_{II})}\right]. \tag{2.5}$$

In Eq. (2.5) we have ordered the factors to facilitate the following three-step interpretation of intercage motion: First benzene must jump to a W site, probably from an S_{II} site, with the rate coefficient $k(\mathrm{S}_{II}\to\mathrm{W})$. Second, benzene must eventually proceed through the W site, with a probability of one half because of relaxation at the W site. Third, benzene must eventually reside in the adjacent cage; the factor $3[1 + k(\mathrm{W}\to\mathrm{W})/\, k(\mathrm{W}\to\mathrm{S}_{II})]$ counts the number of thermally allowed target sites in the new cage. To further clarify the role of this last factor, we consider in Sec. II B various limits of the quantity $\alpha(T) \equiv k(\mathrm{W}\to\mathrm{W})/k(\mathrm{W}\to\mathrm{S}_{II})$.

It is interesting to compare Eq. (2.5) with our previously reported formula for k obtained by fitting the temperature dependence of kinetic Monte Carlo simulation results.[4,5] The temperature dependence of k was fitted to $k(\mathrm{S}_{II}\rightarrow \mathrm{W})\cdot \frac{1}{2}\cdot 4$, where the factor of 4 was thought to account for the four ways to leave the supercage through one of the four windows. Equation (2.5) replaces the factor of 4 with $3[1+\alpha(T)]$, thereby changing our picture of cage-to-cage motion both quantitatively and qualitatively. We now view the cage-to-cage rate coefficient as being proportional to a ''target site factor,'' i.e., the number of thermally allowed target sites in the new cage; rather than being proportional to a ''window factor,'' i.e., the constant number of threshold sites connecting adjacent supercages. Regarding quantitative effects, Eq. (2.5) agrees perfectly with our simulation data as discussed in Sec. III.

Before discussing limits of $\alpha(T)$, we give one further interpretation for our new intercage rate formula starting from Eq. (2.4). The mean supercage residence time, $\langle \tau\rangle_{\mathrm{cage}}=1/k$, can be expressed as

$$\langle \tau\rangle_{\mathrm{cage}}=K_{\mathrm{eq}}(\mathrm{W}\rightarrow \mathrm{S}_{II})\cdot 2\cdot \langle \tau\rangle_W \tag{2.6}$$

$$=\frac{N_{S_{II}}\langle \tau\rangle_{S_{II}}}{N_W\langle \tau\rangle_W}\cdot 2\cdot \langle \tau\rangle_W$$

$$=\langle \tau\rangle_{S_{II}}\cdot \frac{N_{S_{II}}}{N_W}\cdot 2, \tag{2.7}$$

where $N_{S_{II}}$ is the number of visits to S_{II} sites and $\langle \tau\rangle_{S_{II}}$ is the mean S_{II} site residence time. The ratio $N_{S_{II}}/N_W$ counts the average number of jumps in a cage required for benzene to visit a W site. The product $\langle \tau\rangle_{S_{II}}\cdot N_{S_{II}}/N_W$ is thus the average time required for benzene to visit a W site. The factor of 2 accounts for randomizing in the W site which doubles the average time spent in each supercage. Equation (2.7) clarifies the following subtle point: While it is plausible to conclude from Eq. (2.7) that supercage residence times depend upon $\langle \tau\rangle_{S_{II}}$, which in turn is a function of $k(\mathrm{S}_{II}\rightarrow \mathrm{S}_{II})$, the overall cage-to-cage rate coefficient turns out to be *independent* of $k(\mathrm{S}_{II}\rightarrow \mathrm{S}_{II})$. Equations (2.6) and (2.7) demonstrate that the factor $N_{S_{II}}/N_W$, which depends upon all four fundamental rate coefficients, converts the $\langle \tau\rangle_{S_{II}}$ dependence into $\langle \tau\rangle_W$ dependence. As such, while Eq. (2.7) is useful for picturing cage-to-cage motion, and in fact lies most closely to the heart of kinetic Monte Carlo simulations, it does not explicitly reveal how $\langle \tau\rangle_{\mathrm{cage}}$ depends upon fundamental rate coefficients.

C. Limits of $\alpha(T)$

To elucidate the target site factor $3[1+\alpha(T)]$, we consider various limits of $\alpha(T)\equiv k(\mathrm{W}\rightarrow \mathrm{W})/k(\mathrm{W}\rightarrow \mathrm{S}_{II})$ in Eq. (2.5).

1. $\alpha(T)\ll 1$

This limit can be achieved at low temperatures with our present activation energies $E_a(\mathrm{W}\rightarrow \mathrm{W})$ = 18 kJ mol^{-1} and $E_a(\mathrm{W}\rightarrow \mathrm{S}_{II})$ = 16 kJ mol^{-1}. In this case a molecule that has reached the W site will most likely jump to an S_{II} site, either in the old or new cage. There are three such S_{II} sites in the new cage, hence giving a factor of 3 thermally allowed target sites for cage-to-cage motion, i.e., $3[1+\alpha(T)]\cong 3$. We note that this limit also arises by excluding entirely the W→W process as discussed in Sec. III.

2. $\alpha(T)\cong 1$

This limit can be achieved at high temperatures with our present activation energies. In this case a molecule that has reached the W site has equal probability of jumping to an S_{II} or W site. There are six such sites in the new cage, hence giving a factor of 6 thermally allowed target sites for cage-to-cage motion, i.e., $3[1+\alpha(T)]\cong 6$.

3. $\alpha(T)\gg 1$

This limit cannot be achieved with our present rate coefficients for benzene in Na-Y at infinite dilution, but might be possible for benzene loadings near 4 molecules per supercage. In this case, with most S_{II} sites occupied by benzene, a molecule in a W site executing cage-to-cage motion is likely to jump to another W site *before* an S_{II} site in an adjacent cage becomes vacant. This situation is reminiscent of interstitial diffusion,[1] wherein S_{II} sites are lattice positions and W sites are interstitial positions. This limit is interesting because it drastically changes the parameters that control cage-to-cage motion. In this case Eq. (2.5) reduces to

$$k=k(\mathrm{S}_{II}\rightarrow \mathrm{W})\cdot \frac{3}{2}\cdot \frac{k(\mathrm{W}\rightarrow \mathrm{W})}{k(\mathrm{W}\rightarrow \mathrm{S}_{II})}$$

$$=K_{\mathrm{eq}}(\mathrm{S}_{II}\rightarrow \mathrm{W})\cdot k(\mathrm{W}\rightarrow \mathrm{W})\cdot 3. \tag{2.8}$$

Equation (2.8) can be understood by recognizing that in the present limit mobility arises from hopping among interstitial lattice positions only. As such, the cage-to-cage rate coefficient is proportional to $K_{\mathrm{eq}}(\mathrm{S}_{II}\rightarrow \mathrm{W})$, a measure of the fraction of molecules occupying interstitial lattice positions; and is proportional to $k(\mathrm{W}\rightarrow \mathrm{W})$, the mobility coefficient on the interstitial lattice. The factor of 3 counts the number of W →W cage-to-cage jumps from a given W site.

To estimate the overall temperature dependence of k assuming Arrhenius behavior, i.e., $k=\nu e^{-\beta E_a}$, we decompose the individual factors in Eq. (2.8) according to[12]

$$k(\mathrm{W}\rightarrow \mathrm{W})=\nu_{WW}e^{-\beta E_a(W\rightarrow W)}$$

$$=\frac{\omega_{WW}}{2\pi}\cdot e^{(S^{\ddagger}_{WW}-S_W)/k_B}\cdot e^{-\beta(E^{\ddagger}_{WW}-E_W)}, \tag{2.9}$$

$$K_{\mathrm{eq}}(\mathrm{S}_{II}\rightarrow \mathrm{W})=e^{-\beta(F_W-F_{S_{II}})}$$

$$=e^{(S_W-S_{S_{II}})/k_B}\cdot e^{-\beta(E_W-E_{S_{II}})}. \tag{2.10}$$

In Eq. (2.9) E_W and S_W are the internal energy and entropy, respectively, of the W site; $E^{\ddagger}_{WW}$ and $S^{\ddagger}_{WW}$ are the internal energy and entropy, respectively, of the W→W transition state; and ω_{WW} is the vibrational frequency of benzene in the W site along the W→W reaction coordinate. This decomposition of $k(\mathrm{W}\rightarrow \mathrm{W})$ derives from transition state theory using the Helmholtz free energy.[12] In Eq. (2.10) F_W and $F_{S_{II}}$ are the Helmholtz free energies of W and S_{II} sites, respectively;

and $E_{S_{II}}$ and $S_{S_{II}}$ are the internal energy and entropy, respectively, of the S_{II} site. By multiplying Eqs. (2.9) and (2.10) and separating terms we find that

$$\nu = \frac{3\omega_{WW}}{2\pi}\cdot e^{(S^{\ddagger}_{WW}-S_W)/k_B}\cdot e^{(S_W-S_{S_{II}})/k_B}$$

$$= \frac{3\omega_{ww}}{2\pi}\cdot e^{(S^{\ddagger}_{WW}-S_{S_{II}})/k_B}, \tag{2.11}$$

$$E_a = (E^{\ddagger}_{WW}-E_W)+(E_W-E_{S_{II}})$$

$$= E^{\ddagger}_{WW}-E_{S_{II}}. \tag{2.12}$$

These results indicate that diffusion in the limit $\alpha(T)\gg 1$ involves a composite process, since neither ν nor E_a corresponds to a fundamental hopping process. Indeed, the striking conclusion drawn from Eq. (2.12) is that diffusion in this limit is *independent* of the $E^{\ddagger}_{S_{II}W}$ transition state energy, an intriguing result that could not have been predicted from our previously reported formula, $k=\frac{1}{2}\cdot 4\cdot k(S_{II}\rightarrow W)$.[4,5]

We close our discussion of interstitial diffusion by interpreting $3[1+\alpha(T)]$ when $\alpha(T)\gg 1$, which will further elucidate why the intercage rate coefficient is independent of the $E^{\ddagger}_{S_{II}W}$. When $\alpha(T)$ is between zero and one, $3[1+\alpha(T)]$ counts the number of target sites in a new cage. The corresponding interpretation when $\alpha(T)\gg 1$ follows from

$$3[1+\alpha(T)] = 3\left[1+\frac{k(W\rightarrow W)}{k(W\rightarrow S_{II})}\right]$$

$$= 3\left\{\frac{6[k(W\rightarrow S_{II})+k(W\rightarrow W)]}{6k(W\rightarrow S_{II})}\right\}$$

$$= 3/P(W\rightarrow S_{II})$$

$$= 3\cdot N(W\rightarrow S_{II}), \tag{2.13}$$

where $P(W\rightarrow S_{II})$ is the probability of jumping to an S_{II} site while diffusing on the interstitial lattice. As such, $N(W\rightarrow S_{II}) = 1/P(W\rightarrow S_{II})$ is the average number of jumps on the interstitial lattice before relaxing to an S_{II} site. This further elucidates why the interstitial cage-to-cage rate coefficient is independent of $E^{\ddagger}_{S_{II}W}$, namely when $E^{\ddagger}_{S_{II}W} > E^{\ddagger}_{WW}$, the long time spent at S_{II} sites required to occupy W sites is exactly compensated by the long time spent diffusing among W sites, i.e., the product $k(S_{II}\rightarrow W)\cdot N(W\rightarrow S_{II})$ is independent of $E^{\ddagger}_{S_{II}W}$. These long S_{II} and W residence times are related by detailed balance, as evidenced by the equilibrium coefficient in Eq. (2.8).

The kinetic picture is as follows: in the limits that $E_{S_{II}}\ll E_W$ and $E^{\ddagger}_{S_{II}W}\gg E^{\ddagger}_{WW}$, a benzene molecule spends most of its time at S_{II} sites hopping to other S_{II} sites in the *same* supercage, i.e., not contributing to diffusion. Occasionally an $S_{II}\rightarrow W$ hop occurs, placing benzene on the interstitial lattice. Since the activation energies satisfy $E^{\ddagger}_{S_{II}W} > E^{\ddagger}_{WW}$, benzene is more likely to execute $W\rightarrow W$ hops than $W\rightarrow S_{II}$ hops, i.e., benzene diffuses on the interstitial lattice. Eventually benzene relaxes to an S_{II} site where it continues its intracage, $S_{II}\rightarrow S_{II}$ motion. Detailed balance is satisfied, although in an intriguing bifurcation of long, immobile times hopping among S_{II} sites and short, highly mobile durations hopping among W sites.

Further calculations are required to determine if this interstitial limit is actually realized for diffusion in heavily loaded zeolites.[13]

III. SIMULATION METHODOLOGY AND RESULTS

In Sec. II we developed an essentially exact, analytical treatment of benzene diffusion in Na-Y. While the results we obtained were quite plausible, it is comforting to further validate them by carrying out appropriate simulations. Alternatively, one can regard these calculations as tests to determine whether the simulations are sufficiently well converged to give the long time limits in Eqs. (2.1) and (2.2).

A. Kinetic Monte Carlo

We apply the kinetic Monte Carlo (KMC) algorithm[4,5,14–16] to benzene diffusion in Na-Y by replacing the zeolite framework with a three-dimensional lattice of S_{II} and W binding sites. Such a lattice model is known to accurately reproduce diffusive behavior when site residence times are much longer than travel times between sites.[15,17] The probability to make a particular hop from the set ($S_{II}\rightarrow S_{II}$, $S_{II}\rightarrow W$, $W\rightarrow S_{II}$ and $W\rightarrow W$) is proportional to the associated rate coefficient. A hop is made every KMC step[18] and the system clock is updated accordingly. The mean time elapsed before each hop is the inverse of the *total* rate coefficient to leave the originating site.[18] For example, if benzene hops from an S_{II} site, the mean time elapsed is

$$\langle\tau\rangle_{S_{II}} = \frac{1}{3[k(S_{II}\rightarrow S_{II})+k(S_{II}\rightarrow W)]}, \tag{3.1}$$

where the factor of 3 counts available target sites in the Na-Y supercage structure. Since the rate coefficients for leaving the S_{II} site are typically much smaller than those for leaving the W site, the elapsed S_{II} time is much larger than the elapsed W time. As such, the KMC random walk algorithm efficiently models both sluggish and rapid motions in the Na-Y–benzene system. Ensemble averages required for calculating mean supercage residence times are performed as previously described in Ref. 5.

In Refs. 4, 5, 8 and 9 and in the present study, we estimate rate coefficients using the Arrhenius formula, in which $k\cong\nu e^{-\beta E_a}$ where ν and E_a are temperature independent. We assume that the Arrhenius prefactors $\{\nu\}$ resemble typical vibrational frequencies, of order $10^{13}\ \mathrm{s}^{-1}$. We believe these rate coefficients are sufficiently accurate for the purpose of drawing qualitative conclusions. The calculated hopping activation energies and hypothetical Arrhenius prefactors reported in Ref. 4 are summarized in Table I. The calculations that follow use several parameter sets to obtain various limits of the intercage rate coefficient. The parameters in Table I serve as the reference from which other parameter sets are obtained. We note that leaving the W site is much more facile than leaving the S_{II} site with the parameters in Table I. Indeed, the predicted 300 K residence time at the S_{II} site is

TABLE I. Hopping activation energies and hypothetical Arrhenius prefactors for benzene in Na-Y. Our model predicts that leaving the W site is relatively facile.

Jump	Activation Energy (kJ mol^{-1})	Arrhenius Prefactor (s^{-1})
$S_{II} \to S_{II}$	35	10^{13}
$S_{II} \to W$	41	10^{13}
$W \to S_{II}$	16	10^{13}
$W \to W$	18	10^{13}

more than 5000 times longer than at the W site. Reference 4 discusses the detailed hopping mechanisms, in addition to the reasonable agreement between our activation energies and those measured experimentally.

B. Simulation Results

Figure 4 shows an Arrhenius plot of $k_{\rm sim}$, the KMC calculated cage-to-cage rate coefficient. In order to demonstrate the systematic error between simulation and our old theory,[5] we plot in Fig. 4 the quantity $[k_{\rm sim}/\frac{1}{2}\cdot k(S_{II} \to W)] - 3$. Because our old theory asserted that $k_{\rm sim} = \frac{1}{2}\cdot 4\cdot k(S_{II} \to W)$, the quantity plotted in Fig. 4 would equal unity by our old theory. Instead, Fig. 4 demonstrates Arrhenius temperature dependence for $[k_{\rm sim}/\frac{1}{2}\cdot k(S_{II} \to W)] - 3$, indicating that additional rate process(es) control diffusion.

Figure 5 shows $k_{\rm sim}/\frac{1}{2}\cdot k(S_{II} \to W)$, a ‘‘window factor’’ that would equal 4 with our previous theory, plotted against $1000/T$. The solid dots are KMC data including all jumps, while the open dots are obtained from KMC by excluding the W→W jump process. Since excluding the W→W jump changes the cage-to-cage rate coefficient, Fig. 5 suggests that this jump contributes to diffusion in some way. Figures 4 and 5 clearly demonstrate that our previous theory for k is unable to account for the actual temperature dependence of diffusion.

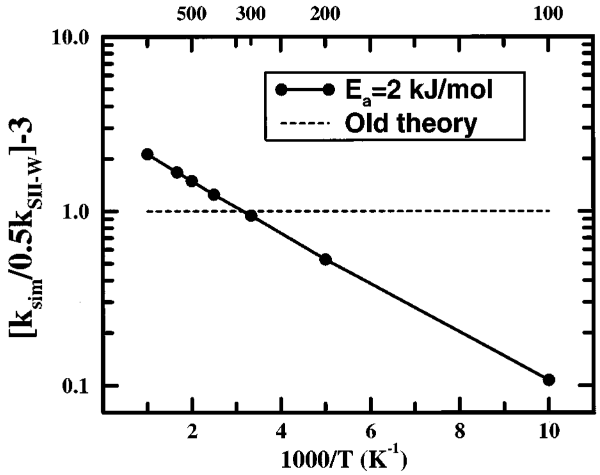

FIG. 4. Arrhenius plot comparing kinetic Monte Carlo calculated cage-to-cage rate coefficients to the $S_{II} \to W$ rate coefficient. The old theory predicts this should be constant, while simulation demonstrates Arrhenius temperature dependence, suggesting that additional rate process(es) control diffusion.

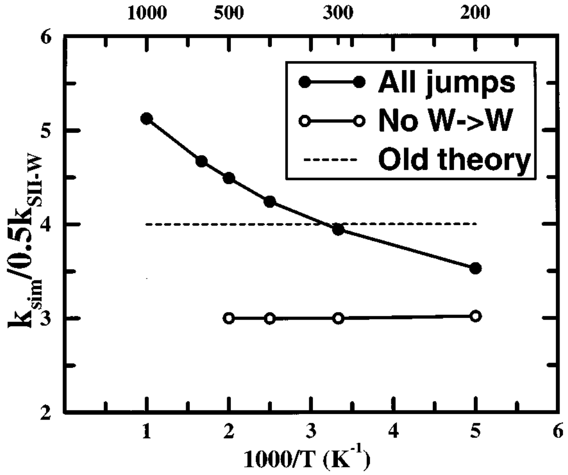

FIG. 5. Temperature dependence of kinetic Monte Carlo calculated cage-to-cage rate coefficients with and without the W→W jump, indicating that this jump process affects diffusion.

According to our new model the quantity plotted in Fig. 4 is $3\alpha(T)$. Since our previous hopping path calculations[4] give $E_a(W \to W) = 18$ kJ mol^{-1} and $E_a(W \to S_{II}) = 16$ kJ mol^{-1}, our new theory predicts that $3\alpha(T)$ should exhibit a 2 kJ mol^{-1} ‘‘activation energy,’’ in perfect agreement with simulation. Furthermore, the quantity plotted in Fig. 5 is $3[1+\alpha(T)]$ which should take the value 3 when excluding the W→W process, again in perfect agreement with simulation. As such, our new formula for benzene diffusion in Na-Y completely resolves the qualitative and quantitative discrepancies between theory and simulation.

In the remaining results we use kinetic Monte Carlo to calculate cage-to-cage rate coefficients at $T = 300$ K using various sets of system parameters. These rate coefficients are reported below in units of the rate obtained from Eq. (2.5) with the parameters in Table I, i.e. in units of $k_{\rm ref} = 1.73\times 10^6$ s^{-1}. Unless otherwise specified, the results below use the parameters in Table I. Table II shows the results of simulations consisting of 3×10^6 KMC steps, each requiring ~7 CPU min on an IBM RS/6000 3AT. In Table II, $k_{\rm sim}$ is the KMC simulated cage-to-cage rate coefficient, $k_{\rm theo}$ is calculated analytically from Eq. (2.5), and $k_{\rm old}$ is our previously reported theory,[5] giving $k = 2k(S_{II} \to W)$. Parameter sets 1 and 2 give $\alpha(T) < 1$ while sets 3 and 4 give $\alpha(T) \gg 1$. Set 1 is precisely that from Table I, which is why in this case $k_{\rm theo}/k_{\rm ref}$ is exactly one.

These simulations give results in nearly exact agreement with our analytical theory over a wide range of parameters, indicating that the simulations have indeed attained the long time limits in Eqs. (2.1) and (2.2), requiring hundreds to thousands of cage-to-cage jumps. Although our old theory appears to be useful for sets 1 and 2, Figs. 4 and 5 show that this agreement at $T = 300$ K is fortuitous because the old theory gives systematic error at other temperatures. Table II shows that with sets 1 and 2 the intercage rate is proportional to $\nu(S_{II} \to W)$ and hence $k(S_{II} \to W)$; while with sets 3 and 4 the intercage rate is roughly proportional to $\nu(W \to W)$ and

TABLE II. Comparison of kinetic Monte Carlo simulations and analytical theory with energies in kJ mol^{-1} and prefactors in s^{-1}, showing quantitative agreement between simulation and our new theory. In sets 1 and 2, $E_a(\mathrm{W}\rightarrow\mathrm{S}_{II}) < E_a(\mathrm{W}\rightarrow\mathrm{W}) = 18$ kJ mol^{-1} and intercage motion is controlled by $k(\mathrm{S}_{II}\rightarrow\mathrm{W})$; while in sets 3 and 4, $E_a(\mathrm{W}\rightarrow\mathrm{S}_{II}) > E_a(\mathrm{W}\rightarrow\mathrm{W})$ and intercage motion is also controlled by $k(\mathrm{W}\rightarrow\mathrm{W})$.

Parameter	Set 1	Set 2	Set 3	Set 4
$E_a(\mathrm{S}_{II}\rightarrow\mathrm{W})$	41	41	50	50
$E_a(\mathrm{W}\rightarrow\mathrm{S}_{II})$	16	16	25	25
$\nu(\mathrm{S}_{II}\rightarrow\mathrm{W})$	10^{13}	10^{12}	10^{13}	10^{13}
$\nu(\mathrm{W}\rightarrow\mathrm{W})$	10^{13}	10^{13}	10^{13}	10^{14}
$\alpha(T)$	0.313	0.313	15.0	150
$k_{\mathrm{sim}}/k_{\mathrm{ref}}$	1.00	0.100	0.257	2.39
$k_{\mathrm{theo}}/k_{\mathrm{ref}}$	1	0.100	0.255	2.40
$k_{\mathrm{old}}/k_{\mathrm{ref}}$	1.02	0.102	0.021	0.021

hence $k(\mathrm{W}\rightarrow\mathrm{W})$ [cf. Eq. (2.8)]. This is predicted by our present treatment but is completely missed by our old theory. Thus, our comparisons between theory and simulation provide further evidence that we have solved the diffusion problem in Na-Y with an exact, analytical treatment.

IV. CONCLUDING REMARKS

We have developed an analytical expression for the diffusion coefficient of benzene in Na-Y at infinite dilution in terms of fundamental rate coefficients, which has been confirmed by extensive kinetic Monte Carlo simulations. This model assumes that benzene jumps among S_{II} and W binding sites, located near Na$^+$ ions in 6-rings and in 12-ring windows, respectively. Our diffusion theory is based on the formula $D=\frac{1}{6}ka^2$ where $a\cong 11$ Å is the intercage length and k is the cage-to-cage rate coefficient. In this article we have determined that k is given by $k(\mathrm{S}_{II}\rightarrow\mathrm{W})\cdot\frac{1}{2}\cdot 3[1+k(\mathrm{W}\rightarrow\mathrm{W})/k(\mathrm{W}\rightarrow\mathrm{S}_{II})]$, a finding that has resolved persistent discrepancies between theory and simulation, and has suggested new interpretations of benzene diffusion in Na-Y. In particular, when $\alpha(T)\equiv k(\mathrm{W}\rightarrow\mathrm{W})/k(\mathrm{W}\rightarrow\mathrm{S}_{II})$ is between zero and one, the factor $3[1+\alpha(T)]$ counts the number of thermally allowed target sites for cage-to-cage motion. Alternatively, when $\alpha(T)\gg 1$ benzene mobility in Na-Y is interpreted as interstitial diffusion, a situation that may arise with loadings of four molecules per supercage. In this case k is controlled by the probability of W site occupancy multiplied by the rate of W→W jump processes. Further calculations are required to determine if interstitial diffusion is actually predicted for benzene in heavily loaded Na-Y.

Since analytical theories are more desirable in terms of computational effort than simulations, one wonders whether the results presented herein can be extended to, e.g., benzene diffusion in Na-Y at finite loadings or indeed other host–guest systems as well. The analogous treatment of diffusion through one-dimensional channel zeolites at infinite dilution is trivial, as we have previously discussed.[5] Extending our approach to, e.g., diffusion in ZSM-5 is however non-trivial and warrants further study. Treating systems with finite loadings is likewise non-trivial, possibly requiring a mean field *ansatz* to establish the equation $D=(1/2d)k_\theta a_\theta^2$, since it is known that single file transport in heavily loaded channel zeolites gives anomalous diffusion.[19,20] Further study is required to determine how widely applicable the methods presented herein are to transport problems in zeolite molecular sieves.

Note added in proof. We have recently developed an analytical theory for the concentration dependence of benzene diffusion in Na–Y based on Eq. (2.3). The results will be reported in a forthcoming publication.[10]

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[1] J. Kärger and D. M. Ruthven, *Diffusion in Zeolites and Other Microporous Solids* (Wiley, New York, 1992).
[2] J. Weitkamp, in *Catalysis and Adsorption by Zeolites*, edited by G. Olhmann, J. C. Vedrine, and P. A. Jacobs (Elsevier, Amsterdam, 1991).
[3] J. M. Newsam, *Solid State Chemistry: Compounds*, edited by A. K. Cheetham and P. Day (Oxford University, Oxford, 1992), pp. 234–280.
[4] S. M. Auerbach, N. J. Henson, A. K. Cheetham, and H. I. Metiu, J. Phys. Chem. **99**, 10 600 (1995).
[5] S. M. Auerbach and H. I. Metiu, J. Chem. Phys. **105**, 3753 (1996).
[6] A. N. Fitch, H. Jobic, and A. Renouprez, J. Phys. Chem. **90**, 1311 (1986).
[7] R. C. Tolman, *The Principles of Statistical Mechanics* (Oxford University, New York, 1938).
[8] S. M. Auerbach, L. M. Bull, N. J. Henson, H. I. Metiu, and A. K. Cheetham, J. Phys. Chem. **100**, 5923 (1996).
[9] S. M. Auerbach and H. I. Metiu, J. Chem. Phys. **106**, 2893 (1997).
[10] C. Saravanan and S. M. Auerbach (in preparation).
[11] H. Klein, C. Kirschhock, and H. Fuess, J. Phys. Chem. **98**, 12 345 (1994).
[12] D. Chandler, J. Chem. Phys. **68**, 2959 (1978).
[13] S. M. Auerbach (in preparation).
[14] K. A. Fichthorn and W. H. Weinberg, J. Chem. Phys. **95**, 1090 (1991).
[15] R. L. June, A. T. Bell, and D. N. Theodorou, J. Phys. Chem. **95**, 8866 (1991).
[16] H. I. Metiu, Y. T. Lu, and Z. Y. Zhang, Science **255**, 1088 (1992).
[17] R. Gomer, Rep. Prog. Phys. **53**, 917 (1990).
[18] P. Maksym, Semicond. Sci. Technol. **3**, 594 (1988).
[19] V. Kukla *et al.*, Science **272**, 702 (1996).
[20] K. Hahn, J. Kärger, and V. Kukla, Phys. Rev. Lett. **76**, 2762 (1996).