

A combined quantum-classical dynamics method for calculating thermal rate constants of chemical reactions in solution

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We present a combined quantum-classical-stochastic dynamics method based on the flux-flux correlation function for calculating the thermal rate constants of chemical reactions in solution or in biological systems. The present method is an extension of an earlier method by Metiu and co-workers [J. Chem. Phys. **88**, 2478 (1988)] to include stochastic dynamics. The method is tested by applying it to a simple model of hydrogen atom transfer reaction in solution. We also examine the behavior of the flux-flux correlation function and the rate constants as functions of viscosity.

I. INTRODUCTION

Although computer technologies have advanced significantly in the past decade, full quantum-mechanical dynamics calculations are still limited to systems with a few degrees of freedom.¹⁻⁵ Even with anticipated increases in computer performance, such calculations for important processes such as proton transfer in proteins are far from tractable. At the present time, the only practical method for detailed simulations of biological processes is classical molecular dynamics. However, classical dynamics does not take into account quantum mechanical tunneling, which is a vital process in many biological systems, particularly in proton transfer in proteins.⁶ Some attempts at developing a semiclassical trajectory method⁷ or calculating the quantum corrections⁸ for these processes have been reported. Recently, Borgis and Hynes⁹ have proposed a quantum transition state theory for proton transfer reactions in solution, although applications of this method to enzymes have not yet been carried out. From a different point of view, the development of a mixed quantum-classical dynamics method in which a small number of atoms in the system are treated quantum mechanically while the remaining atoms are treated classically, would be a reasonable approach. Several methods^{10,16} attempting to combine classical and quantum dynamics have been proposed and have shown some encouraging results for surface diffusion,^{10,11} dissociation on metals,¹² photodissociation in solid processes,¹³ colinear bimolecular gas-phase reactions,¹⁴ and also for proton transfer reactions in solution.¹⁶ It is worthwhile to mention that also in this spirit, several methods^{17,18} have been described that attempt to combine molecular orbital theory with molecular mechanics to give information about the potential energy surface of chemical reaction in macromolecules such as in proteins. Such methods in conjunction with a combined quantum-classical dy-

namics method such as the one proposed in this study would provide a complete tool for studying the quantum dynamics of chemical reactions in biological systems.

Our goal is to develop a mixed quantum-classical dynamics method that enables us to investigate quantum mechanical processes in biological systems such as proton or hydrogen atom transfer in proteins. Such a method should also be general enough that it can be applied to reactions in solutions, in zeolites, or in polymers. In the present paper, we extend the mixed quantum-classical dynamics method proposed by Wahnström, Carmeli, and Metiu¹⁰ (WCM) to include stochastic dynamics for treatments of reactions in solutions. This method is based on a flux-flux correlation formalism^{19,20} for calculating the thermal chemical reaction rate constants. Furthermore, we also employ an efficient and accurate quantum mechanical time evolution method, namely the kinetic referenced modified Cayley method,^{21,22} to propagate the wave function in time under the influence of a time dependent potential. To test the present method, we apply it to a simple model hydrogen atom transfer reaction in solution which has the potential energy interaction represented by a one-dimensional double-well potential coupled to a harmonic bath.²³ We examine the behavior of the flux-flux correlation function and the calculated rate constants as functions of both temperature and solvent viscosity. Applications of the present method to proton or hydrogen atom transfer reactions in solutions are in principle straightforward, but require more realistic potential energy functions which are subjects of current research.

In Sec. II, we review the basic formulation of the flux-flux correlation function method for calculating the thermal rate constants in mixed quantum-classical dynamics, as proposed by Metiu and co-workers, and we emphasize the modifications made in the present study. The model potential energy function for the hydrogen atom transfer reaction in solution and the details of the dynamical calculations are given in Sec. III. Section IV gives results and discussion.

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II. THEORY

In the present study, we consider molecular systems in which one atom requires quantum mechanical treatment while the remaining can be treated classically. For simplicity, we assume the quantum atom has only one degree of freedom denoted as x and its conjugate momentum p . Furthermore, we assume that x is also the reaction coordinate. The remaining N one-dimensional spectator particles, whose coordinates and momenta are denoted by R and P , will be treated classically. Generalizing the present formalism to three-dimensional particles is straightforward.

The rate constant k of a chemical reaction for a quantum system under thermal conditions can be expressed in terms of various correlation functions.^{19,20} For this study, we use the Miller, Schwartz, and Tromp²⁰ expression given by

$$kQ_r = \int_0^\infty C_{ff}(t) dt, \quad (1)$$

where Q_r is the reactant partition function. The flux-flux correlation function C_{ff} calculated at the dividing surface $x = x_0$ is given by

$$C_{ff}(t) = \left(\frac{\hbar^2}{2m^2}\right) \text{Re} \left(\frac{\partial}{\partial x_1} \frac{\partial}{\partial x_2} - \frac{\partial}{\partial x_3} \frac{\partial}{\partial x_1} \right) \times \text{Tr}_s \{ \langle x_3 | U | x_4 \rangle^* \langle x_1 | U | x_2 \rangle \}, \quad (2)$$

where x_1, x_2, x_3 , and x_4 are set equal to x_0 after performing the derivatives. Tr_s is the trace over the spectator variables R , and the U operator is defined as

$$U = e^{(-i\mathbf{H}t/\hbar)} e^{(-\beta\mathbf{H}/2)}, \quad (3)$$

where \mathbf{H} is the total Hamiltonian operator, t is the time, and β is $(k_b T)^{-1}$ with k_b the Boltzmann constant and T the temperature. Equations (1)–(3) define an exact quantum mechanical expression of the rate constant in terms of the flux-flux correlation function. WCM have proposed a procedure to treat the spectator degrees of freedom classically, and it is described in the following.

First, we assume that the total Hamiltonian can be written as

$$\mathbf{H} = \mathbf{h}(\hat{x}, \hat{p}, \hat{R}) + \mathbf{H}_s(\hat{R}, \hat{P}), \quad (4)$$

where \mathbf{h} is the sum of the kinetic energy and potential energy operators of the quantum particle plus its interaction with the classical atoms and \mathbf{H}_s is the Hamiltonian operator for the spectator atoms interacting with each other only, but not with x . Furthermore, we also assume that \mathbf{h} and \mathbf{H}_s commute. Consequently, we can write

$$\text{Tr}_s \{ \langle x_3 | U | x_4 \rangle^* \langle x_1 | U | x_2 \rangle \} = \text{Tr}_s \{ F(t) e^{-\beta\mathbf{H}_s} \}, \quad (5)$$

where

$$F(t) = e^{(i\mathbf{H}_s t/\hbar)} \{ \langle x_3 | \mathbf{u} | x_4 \rangle^* \langle x_1 | \mathbf{u} | x_2 \rangle \} e^{(-i\mathbf{H}_s t/\hbar)}, \quad (6)$$

and

$$\mathbf{u} = e^{(-i\mathbf{h}t/\hbar)} e^{(-\beta\mathbf{h}/2)}. \quad (7)$$

Note that $F(t)$ is still an operator acting over the space of the spectator degrees of freedom.

The next step is to take the classical limits over the spectator space. To do these, we replace the trace by its corresponding integral over the spectator classical phase space,

and the coordinate and conjugate momentum operators, \hat{R} and \hat{P} , by the corresponding classical trajectories $R(t)$ and $P(t)$. Consequently, Eq. (2) becomes

$$C_{ff}(t) = \left(\frac{\hbar^2}{2m^2}\right) \text{Re} \left(\frac{\partial}{\partial x_1} \frac{\partial}{\partial x_2} - \frac{\partial}{\partial x_3} \frac{\partial}{\partial x_1} \right) \times \int_0^\infty \frac{dR dP}{(2\pi\hbar)^N} e^{(-\beta H_s^c(R,P))} F\{R(t), P(t)\}, \quad (8)$$

where $H_s^c(R,P)$ is the classical Hamiltonian corresponding to \mathbf{H}_s .

WCM have proposed several computational schemes for calculating $F\{R(t), P(t)\}$. In the present study, we propose a new scheme for treatment of reactions in solution. Also, we utilize an efficient and accurate quantum evolution method in the new computation scheme described below.

Computational scheme. In order to calculate $F\{R(t), P(t)\}$, we first consider the matrix element $\langle x_1 | \mathbf{u} | x_2 \rangle$ that appears in Eq. (6), and it can be written as

$$\langle x_1 | \mathbf{u} | x_2 \rangle \equiv \langle x_1 | \psi_t \rangle \equiv \langle x_1 | e^{-i\mathbf{h}t/\hbar} | \phi_\beta \rangle \quad (9)$$

or in ket notation,

$$| \psi_t \rangle = e^{-i\mathbf{h}t/\hbar} | \phi_\beta \rangle. \quad (10)$$

For consistency, in the present study, we use the same notations as in the previous work of WCM. Here ψ_t is the time evolution of the thermal wave function ϕ_β which is defined as

$$\phi_\beta(x) \equiv \langle x | e^{-\beta\mathbf{h}/2} | x_2 \rangle. \quad (11)$$

Thus, the thermal wave function ϕ_β can be calculated by propagating an eigenstate in the coordinate representation through imaginary time to the specified temperature. In our previous study,²² we have found that the (second order) kinetic referenced split operator (KRSO) method is more efficient compared to others in imaginary time evolution of the wave function. Hence, we employ the KRSO method in the present study. Furthermore, when taking the classical limits over the spectator space, $\mathbf{h}(\hat{x}, \hat{p}, \hat{R})$ becomes $\mathbf{h}(\hat{x}, \hat{p}, R)$ where R is just a classical variable. Further details of the KRSO method and the computational procedure for calculating ϕ_β are described in our previous study²² and others.¹⁰

From Eq. (10), ψ_t is obtained by propagating the thermal wave function ϕ_β in time. In particular, we must solve the time dependent Schrödinger equation with the Hamiltonian $\mathbf{h}(\hat{x}, \hat{p}, \hat{R})$ and the initial condition $\phi_\beta(x)$. However, \hat{R} is replaced by its corresponding classical trajectory $R(t)$ when we take the classical limit over the spectator phase space. Thus, the potential energy operator in the Hamiltonian \mathbf{h} becomes a time dependent function. The time dependent Schrödinger equation then has the form,

$$i\hbar \frac{\partial \psi_t}{\partial t} = \mathbf{h}\{\hat{x}, \hat{p}, R(t)\} \psi_t, \quad (12)$$

with the initial condition $\phi_\beta(x)$. Since $\phi_\beta(x)$ also depends on R , it is obvious to impose the initial condition in the spectator classical phase space; i.e., the initial points of the classical trajectories $R(t)$ and $P(t)$, $R(t=0)$ equals R , and $P(t=0)$ equals P , where R and P are the integration variables in Eq. (8). There are several methods available for

solving the time dependent Schrödinger equation with a time independent potential energy function, and we refer to our previous study²² for a detailed discussion of the methodologies and efficiencies of these methods. From that study, we found that the kinetic referenced modified Cayley (KRMC) method is quite efficient in both the computational requirements and accuracy compared to other methods, such as the split operator and Chebychev polynomial expansion methods. Furthermore, the KRMC method does not depend on the form of the potential. Thus, it can treat a time dependent potential such as that in Eq. (12), and hence it is used in the present study. The other two methods on the other hand require the time step to be sufficiently small that the potential energy is effectively invariant over that time period; consequently, they would be computationally expensive for solving Eq. (12).

The time dependent Schrödinger equation above, Eq. (12), yields the time evolution of the thermal wave function $\phi_\beta(x)$. However, it is coupled with the motions of the classical particle(s) (degrees of freedom). Thus, in order to solve Eq. (12) for the wave function ψ_i , we must also simultaneously compute the classical trajectory specified by $R(t)$. Since our goal is to develop a method for studying biological reactions in solution, we must also include solution effects and/or effective motion of protein environment in the dynamics. In the present study, the motions of the classical particle(s) are specified by the Newtonian classical dynamics, whereas solvent motions are implicitly described by the stochastic dynamics. The equation of motion for calculating $R(t)$ is then expressed as

$$M\ddot{R} = -\frac{\partial V_s}{\partial R} - \int \psi_i^*(x) \frac{\partial v_{qs}}{\partial R} \psi_i(x) dx + f_r(t) - M\gamma\dot{R}, \quad (13)$$

where M is the mass of the spectator (classical) particle(s), V_s is the potential energy interactions of the classical particles among themselves but not with the quantum particle, v_{qs} is the potential energy interaction between only the quantum particle and the classical ones, γ is the friction constant, and $f_r(t)$ is the Gaussian random force satisfying the fluctuation-dissipation conditions

$$\langle f_r(t) \rangle = 0, \quad \langle f_r(t) f_r(0) \rangle = 2M\gamma k_b T \delta(t). \quad (14)$$

In the present study, we use a variant of the Verlet algorithm proposed by Brünger *et al.*²⁴ in which the classical coordinate at time $t + \tau$, where τ is the time step is determined by

$$R(t + \tau) = \frac{1}{(1 + \frac{1}{2}\gamma\tau)} \left\{ 2R(t) - R(t - \tau) + [G(t) + f_r(t)] \frac{\tau^2}{M} + \frac{1}{2}R(t - \tau)\gamma\tau \right\}, \quad (15)$$

where $G(t)$ is the sum of the first two terms in Eq. (13). The advantage of using this algorithm is that it converts to the normal Verlet algorithm as the friction constant γ goes to zero. Thus, we can calculate rate constants as a function of the solvent viscosity.

From Eqs. (6) and (8), we also need to calculate the quantity $\langle \partial/\partial x_2 \rangle \langle x_1 | u | x_2 \rangle$ which is quite different from

$\langle x_1 | u | x_2 \rangle$ discussed above. Again using the same notation as in WCM, we have the thermal wave function

$$\langle x | \tilde{\phi}_\beta \rangle \equiv \tilde{\phi}_\beta(x) \equiv \langle x_1 | e^{-\beta\hbar/2} \frac{\partial}{\partial x_2} | x_2 \rangle \quad (16)$$

which differs from the thermal wave function $\phi_\beta(x)$ defined in Eq. (11). However, computationally the difference is only in the initial wave function or the first step of the imaginary time propagation, as has been discussed previously.²⁵ We also use the KRMC method to calculate $\tilde{\phi}_\beta$ in this study. Subsequently, the calculation of

$$\langle x_1 | u \frac{\partial}{\partial x_2} | x_2 \rangle \equiv \langle x_1 | \tilde{\psi}_i \rangle \equiv \langle x_1 | e^{-\hbar t/\hbar} | \tilde{\phi}_i \rangle \quad (17)$$

is the same as for ψ_i as discussed above except that the initial condition is $\tilde{\phi}_\beta$ instead of ϕ_β . Note that in this case, it results in a different classical trajectory $\tilde{R}(t)$ since a different wave function is used to calculate the Ehrenfest force in Eq. (13).

In summary, with the new notation Eq. (8) can be rewritten as

$$C_{\mathcal{F}}(t) = \left(\frac{\hbar^2}{2m^2} \right) \text{Re} \int \frac{dR dP}{(2\pi\hbar)^N} e^{\{-\beta H_s^c(R,P)\}} \times \left\{ \psi_i^*(x_0) \frac{\partial}{\partial x_0} \tilde{\psi}_i(x_0) - \left| \frac{\partial \psi_i(x_0)}{\partial x_0} \right|^2 \right\}. \quad (18)$$

Thus, for each classical phase space point (R,P) , we independently and simultaneously calculate the thermal wave functions ϕ_β and $\tilde{\phi}_\beta$ using the KRMC method. Next, we simultaneously solve the time dependent Schrödinger equations using the KRMC method for ψ_i and $\tilde{\psi}_i$ concurrently with integrating the classical equation of motion using Eq. (15) for $R(t)$ and $\tilde{R}(t)$, respectively. The computational flow of the present scheme is quite natural for parallel computers where one can assign two processors for each phase space point (R,P) , one for calculating ψ_i and the other for $\tilde{\psi}_i$. To calculate the integral in Eq. (18), one can use a Monte Carlo method with the Boltzmann factor $\exp\{-\beta H_s^c(R,P)\}$ as a weighting function to generate phase space points (R,P) as proposed earlier by WCM. For a larger number of classical degrees of freedom, a Monte Carlo method would be the method of choice. However, for a small number of classical degrees of freedom such as in the model Hamiltonian used in this study we found it preferable to calculate the integral numerically by the Simpson rule method to avoid questions concerning the convergence of the Monte Carlo method. Thus, we can focus on the influence of combining quantum, classical, and stochastic dynamics on the dynamical result itself.

Note that in the present scheme, the dynamics of the classical degrees of freedom are coupled to the quantum coordinate via the time dependent potential energy interaction. Thus, they do not respond properly to excitations in the quantum space. For the feedback from the quantum part, the force acting on the classical coordinates from the quantum wave function ψ_i is approximated by the Ehrenfest force which is the average over the whole quantum probability distribution. One can raise a concern over the validity of the Ehrenfest model when the system goes through bifurcations.²⁶ In such a case, the correct force should be the aver-

age depending on which quantum state is considered. In other words, verifications of the principle of detailed balance and microscopic reversibility at the interface between the quantum and classical spaces are not obvious. In the present scheme, the stochastic dynamics which describes solvent motions only enters in the classical dynamics formalism as in Eq. (13); thus it directly affects the dynamics of the classical degrees of freedom, and indirectly couples to the quantum ones. The rationale used here is that one simulation approach could consist of three parts.^{27,28} The innermost shell is the quantum part which consists of one or a few atoms, the middle shell is the classical part which consists of atoms whose dynamics are treated explicitly, and the outermost shell is the stochastic part where the dynamics is represented by the statistical fluctuation theory. In this picture, the stochastic shell is only in direct contact with the classical shell. This approach would have to be generalized if the middle shell were not large enough to screen long range interactions between the innermost and outermost regions.

With the concerns raised above, and the approximations in the formalism, it is clear that the present scheme requires careful testing. However, the original WCM quantum-classical method has been carefully tested against exact quantum mechanical calculations for a model Hamiltonian, and successfully applied to hydrogen diffusion on metallic surfaces. Furthermore, we carried out quantum-classical-stochastic wave packet dynamics calculations for proton transfer in the proton bound ammonia dimer $[\text{H}_3\text{N}\cdots\text{H}\text{NH}_3]^+$, proton bound water ammonia complex $[\text{H}_2\text{O}\cdots\text{H}\text{NH}_3]^+$, and malonaldehyde in our previous study,²⁹ and found that the simulation results are in reasonable agreement with available experimental data. Reasonable agreement with experiment is also obtained in our unpublished simulations of H_2^+ where the electron is the quantum particle, and for $[\text{D}\mu\text{T}]^+$ where the muon is the quantum particle.

In the next section, we present the model Hamiltonian for the hydrogen atom transfer reaction and the dynamical results obtained using the method described above.

III. MODEL HAMILTONIAN AND COMPUTATIONAL DETAILS

To demonstrate the computational method, we apply it to a simple two-dimensional Hamiltonian model for a hydrogen atom transfer reaction. In particular, we used the Makri and Miller²³ symmetric double well coupled to a harmonic oscillator model which has the form

$$H = \frac{p_x^2}{2m} + \frac{P^2}{2m} + V_0(x) + \frac{1}{2}m\omega^2 \left[R - \frac{cx^2}{m\omega^2} \right]^2. \quad (19)$$

Here x is the quantum coordinate and also the reaction coordinate. $V_0(x)$ is a symmetric double well potential

$$V_0(x) = -\frac{1}{2}a_0x^2 + \frac{1}{4}c_0x^4. \quad (20)$$

The constants a_0 and c_0 are chosen such that the barrier height is at 0.012 43 hartrees, and the two minima are located at $x = \pm 1.0$ bohr. The mass m is of the hydrogen atom and the harmonic oscillator frequency is set at 298 cm^{-1} . The coupling constant c is set equal to $0.004 \text{ hartrees/bohr}^2$. These parameters are the same as those in Ref. 23 and are

typical of H-atom processes. Furthermore, we have chosen the quadratic coupling case since it yields a potential energy surface similar to those of proton transfer processes we considered in our previous study.²² The potential contour for this potential energy function is shown in Fig. 1.

For dynamics calculations, the reaction or quantum coordinate is discretized using 256 points with the grid size $\Delta x = 0.015$ bohr. The time steps in both real and imaginary time propagation are chosen sufficiently small to ensure the convergence of the calculations. In particular, τ is set to 0.1 fs, and the number of imaginary time steps is 100. We use the kinetic referenced split operator method for the imaginary time quantum propagation, the kinetic referenced modified Cayley method for the real time quantum propagation, and the Verlet algorithm defined in Eq. (15) for the real time classical propagation. The integration over the classical phase space is done numerically using the Simpson rule method with the range and integration step chosen to ensure convergence. For the stochastic part, the friction constant γ is calculated from the Stoke's law

$$\gamma = 6\pi\eta r_h, \quad (21)$$

where η is the solvent viscosity; r_h is the hydrodynamic radius and is set equal to 1 Å in these calculations.

IV. DISCUSSION

We have calculated the rate constants, k_Q , for the temperature range from 200 to 400 K for the hydrogen atom transfer reaction in aqueous solution using the above Hamiltonian model with the water viscosity used in the stochastic dynamics. We also examined the behavior of the rate constant of this hydrogen transfer process with respect to different viscosities.

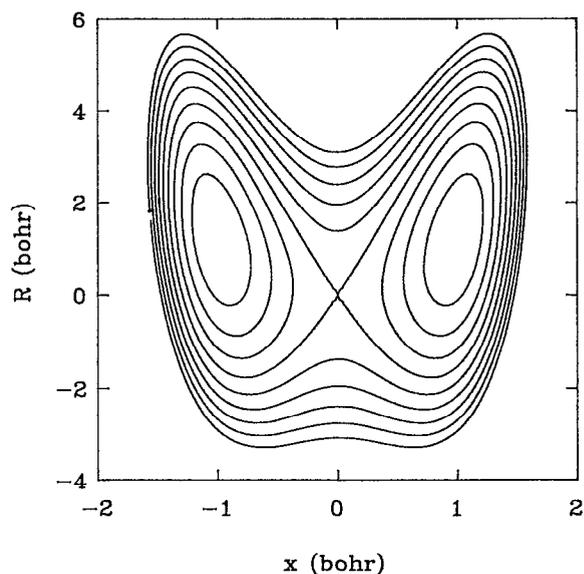


FIG. 1. Equipotential energy contour plot for the Makri and Miller double well potential. Contour levels are from -6 to 10 kcal/mol with the difference of 2 kcal/mol .

First, we discuss the case for hydrogen transfer in aqueous solution. In Fig. 2, we show the flux–flux correlation functions for temperatures $T = 200, 300,$ and 400 K. Note that the flux–flux correlation functions fluctuate but also decay to zero at longer time. Such decay is found to be more rapid at higher temperature. This is due to the fact that there are larger solvent fluctuations at higher temperature, which causes the population to relax at a faster rate. Recall that the solvent fluctuation is modeled by stochastic dynamics in the present method. At lower temperatures, one may need to run longer simulations to ensure that the decaying correlation functions reach zero or a small number. However, there is a limitation of the present method for calculating the rate constants at low temperatures. That is, in calculating the flux–flux correlation function, $C_{ff}(t)$, we start the thermal wave packet at the saddle point and only monitor the flux through the dividing surface, which is perpendicular to the reaction coordinate and intersects it at the saddle point. At low temperatures, the starting thermal wave function is quite delocalized and nearly split in halves over the barrier and further separated as time progresses (see Fig. 5 in the previous study²⁵). In such cases, the validity and accuracy of the Ehrenfest force are questionable. However, since the flux–flux correlation functions decay over a relatively short time, especially at moderate to high temperatures, the errors have much less time to accumulate compared to wavepacket simulation methods, and even if the errors do accumulate, they only contribute to the tails of the correlation functions and thus have a small effect on the rate calculations. The rate constants for this model Hamiltonian and the transmission coefficients, which are calculated by

$$\Gamma(T) = \frac{2\pi}{k_b T} e^{-\beta\Delta V} \int_0^\infty C_{ff}(t) dt, \quad (22)$$

where ΔV is the barrier height, are shown in Table I. The viscosity of water is used in this case. Note that the transmission coefficients increase rapidly as the temperature de-

TABLE I. Calculated transmission coefficients and rate constants (s^{-1}) for a model proton transfer reaction in aqueous solution.

$T(K)$	Γ	kQ_r
200	243.39	3.04(6) ^a
220	83.46	6.83(6)
240	37.01	1.46(7)
260	20.18	3.04(7)
300	9.26	1.20(8)
350	5.46	5.36(8)
400	4.01	1.83(9)

^aPower of ten in parentheses.

creases. Tunneling is found to be very important, even at room temperature, where it enhances the transfer rate by nearly an order of magnitude. The present results are also consistent with those of Rom, Moiseyev, and Lefebvre³⁰ (RML) which are based on a resonance energy formalism. This is in fact very encouraging since both methods involve completely different approaches. The approach of RML, based either on a basis set expansion method or a propagation and matching method for calculating the resonance energy levels, was found to be more accurate at low temperatures, $T < 260$ K, whereas the present method is applicable at moderate to high temperatures, $T > 200$ K. Furthermore, applications of the present method to macromolecules are technically simpler.

We have also examined the behavior of the flux–flux correlation functions at different solvent friction constants. In Fig. 3, we plot the correlation functions calculated at $T = 300$ K for three different solvent viscosities, $\eta = 0.01, 0.89,$ and 100 cP. As the viscosity increases, the decay of the flux–flux correlation function becomes slower. In other words, the system relaxation time increases. This is in fact consistent with our intuitive understanding of chemical reactions in solution. Consequently, the present method suffers the same limitation in calculating the rate constants

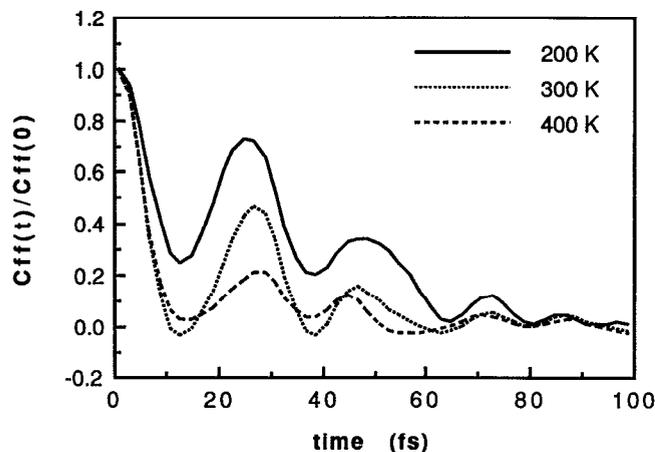


FIG. 2. Normalized flux–flux correlation functions plotted versus time at $T = 200, 300,$ and 400 K for the model hydrogen atom transfer reaction in aqueous solution.

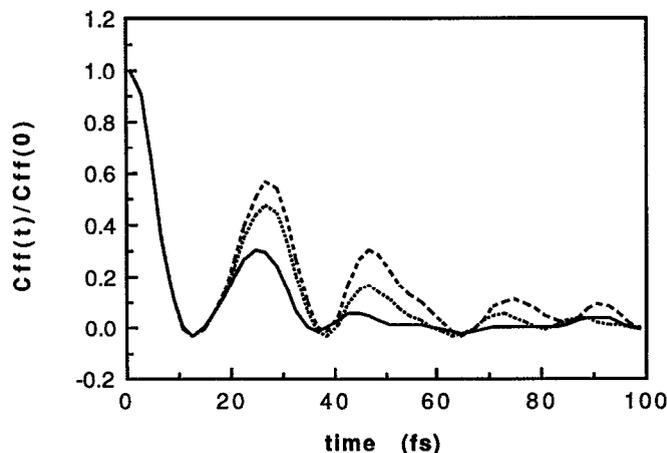


FIG. 3. Normalized flux–flux correlation functions plotted vs time at $T = 300$ K, for three different solvent viscosities, $\eta = 0.01$ (solid line), 0.89 (water, dotted line), and 100 cP (dashed line).

of chemical reactions in solution with very high viscosities as in the case of low temperatures discussed above. It is interesting to note that the correlation functions for different friction constants in Fig. 3 are nearly superimposed in the first 20 fs of the reactive dynamics, and start to differentiate only after that time. A physical explanation for this observation is that the reaction, i.e., hydrogen transfer, takes place on a short time scale while the solvent motions require some time to respond to such changes in the system. This is an important result since it is one of the fundamental assumptions in the continuum theories of proton and electron transfer reactions. The calculated rate constants and transmission coefficients plotted vs the solvent viscosity are shown in Fig. 4. At low friction, the rate constant is found to decrease as the friction decreases. This is in fact similar to Kramer's effect³¹ seen in the classical dynamics of reactions in solution. The transmission coefficients are also found to decrease as the friction decreases in the low friction region. However, both the rate constant and transmission coefficient approach a plateau region as the solvent friction increases up to the level being considered here.

Since biological processes typically occur near room temperature and in aqueous solution, the present combined

quantum-classical-stochastic dynamics method provides a useful and tractable tool for investigating the quantum mechanical effects in such systems. We are now in process of applying the present method to more realistic systems of proton transfer reactions in solution, and eventually to proton transfer in enzymes.

V. CONCLUSION

We have presented a new combined quantum-classical-stochastic dynamics method for studying the dynamics of chemical reactions in solution. The present method is an extension of the Wahnström, Carmeli, and Metiu combined quantum-classical method. It is based on the flux-flux correlation function formalism, for calculating the chemical reaction rate constant. We have tested the present method by applying it to a model Hamiltonian for the hydrogen atom transfer reaction in solution. We have examined the stability of the method with regard to temperature and the viscosity of the solvent. We found that the dynamical results are stable for moderate to high temperatures, $T > 200$ K in the present case, and when the viscosity of the solvent is not very large. Applications of the present method to a more realistic model of proton transfer reactions in proteins are in progress.

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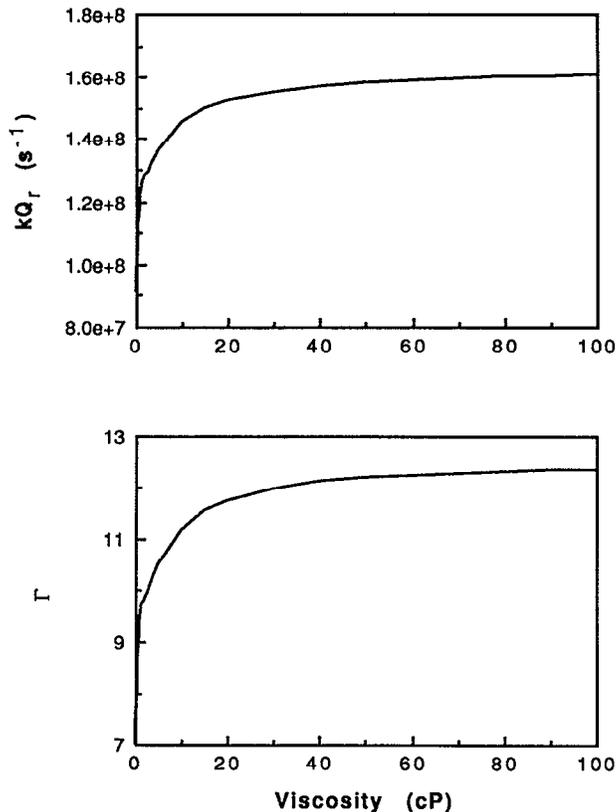


FIG. 4. Rate constants, kQ_r (s^{-1}), and transmission coefficients at room 300 K plotted vs the solvent viscosity (cP).

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