Quantum Dynamical Simulations of Nonadiabatic Processes: Solvation Dynamics of the Hydrated Electron

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A new method for simulating nonadiabatic quantum processes is presented. It is suitable for transitions which are not dominated by near crossing of potential surfaces. The method is applied to the calculation of the radiationless transition rate of the hydrated electron from its lowest excited level to the ground state. The results are consistent with recent experimental indications that this process dominates the solvation dynamics of the electron in water.

The evaluation of nonadiabatic (NA) transition rates in realistic systems has always posed a serious numerical challenge, associated with the fact that one is trying to compute a strongly quantum process in an otherwise essentially classical system. Most of the practical methods used to date are based on the Tully-Preston [1] surface hopping idea and are thus limited to NA processes which are dominated by near crossings of adiabatic potential surfaces. In many processes, e.g., radiationless transitions in large molecules or in impurity centers in solids at low temperatures, the NA transition often occurs in an extended range of phase space, and its rate is dominated by a small Franck-Condon factor. In this Letter we present a new method for calculating such rates. The method is based on running classical trajectories on the initial adiabatic potential surface (here these trajectories are obtained from a mixed quantum-classical evolution where the potential surface is evaluated along the trajectory using the adiabatic simulation method [2]) and on a semiclassical evaluation of the "golden rule" expression for the NA transition rate.

The method is applied to calculating the radiationless transition rate from the lowest excited state of the hydrated electron to the ground state. This application is motivated by recent experimental results on the dynamics of electron solvation in water [3,4]. These works indicate that the formation of the fully hydrated electron goes through at least one intermediate species. Using the simple kinetic model

$$e_{\text{quasifree}} \xrightarrow{k_1} e_{\text{wet}} \xrightarrow{k_2} e_{\text{solvated}} \tag{1}$$
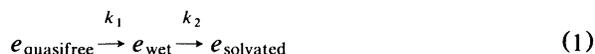
(where $e_{\text{quasifree}}$ is the initially ejected electron and e_{wet} is the intermediate state), Long, Lu, and Eisenthal [4(b)] have fitted their data with $k_1^{-1} = 180 \pm 40$ fs and $k_2^{-1} = 540 \pm 50$ fs. Migus *et al.* [3(a)] have given different estimates: $k_1^{-1} = 110$ fs and $k_2^{-1} = 240$ fs. Also Long, Lu, and Eisenthal [4(b)] have identified an isosbestic point at ~ 820 nm, indicating a process dominated by two-state kinetics. Migus *et al.*, while advocating the

two-state model, have not identified such a point. Finally, Long, Lu, and Eisenthal [4(a)] report a 35% longer rise time for the appearance of the solvated electron in D_2O relative to the same process in H_2O. On the other hand, Gauduel *et al.* [3(c)] report a very small isotope effect $(\tau_{D_2O}/\tau_{H_2O} \sim 1.1)$ on these times.

These observations cannot be accounted for by either molecular theories or by adiabatic molecular simulations. Recent molecular theories [5] indicate that solvent relaxation during charge solvation is nonexponential, characterized by time scales between the longitudinal (τ_L) and the Debye (τ_D) dielectric relaxation times. In water $\tau_L \sim 300$ fs and $\tau_D \sim 10$ ps. In contrast, numerical simulations of both classical charge [6] and *adiabatic* electron solvation [7] in water have shown that a substantial part of the solvation process occurs on a time scale of 20–30 fs. Clearly, neither can account for the observation of the intermediate state "e_{wet}."

Concerning e_{wet}, it is reasonable to assume [4(b),7] that it corresponds to the three closely lying lowest excited p-like states which carry most of the oscillator strength of the 1.7-eV absorption by the fully hydrated electron. If so, k_2 of Eq. (1) is the averaged NA transition rate from these states to the ground state.

Webster and co-workers [8] have recently simulated the NA transitions involving the higher states of the electron in water using the semiclassical theory of Pechukas [9] (estimating k_2^{-1} to be of order ~ 1 ps). This method is based on an iterative determination of the solvent trajectories and is therefore highly CPU demanding. Its applicability when the potential surfaces involved are far from each other throughout the process is unclear, since it leaves open the choice of a coherence time beyond which surface hopping is imposed on the mixed state evolution. Space and Coker [10] have used a method recently proposed by Tully [11] for simulating transitions between the higher excited states of the electron in helium. This method is potentially very useful but its applicability for the present situation of extended NA interaction is yet to be demonstrated.

Our new approach is particularly useful in cases of extended coupling between noncrossing surfaces. In essence, we take advantage of the fact that in such situations, when characterized by large density of final levels, the golden-rule expression for the rate is valid, and we directly evaluate this rate. This method is somewhat similar in spirit, though completely different in implementation, to the semiclassical scheme used by Herman [12] for vibrational relaxation, and it supplements other methods [1,8–11] which focus on populations and coherences in the electronic states themselves.

Our method [13] is based on a direct semiclassical simulation of the golden-rule expression for the transition rate between two electronic states 1 and 2,

$$k_{1\to2}=\frac{2\pi}{\hbar}\sum_i\frac{e^{-\beta E_{1i}}}{Z_1}\sum_f|\langle1i|V|2f\rangle|^2\delta(E_{1i}-E_{2f}),\quad(2)$$

where $Z_1=\sum_i e^{-\beta E_{1i}}$. $|\alpha j\rangle=|\phi_\alpha\rangle|\chi_{\alpha j}\rangle$ $(\alpha=1,2;\ j=i,f)$ are vibronic levels in the initial $(\alpha=1)$ and final $(\alpha=2)$ states, respectively. $\phi_{1(2)}$ are adiabatic electronic states and $\chi_{i(f)}$ are the corresponding vibrational states. The nonadiabatic coupling is approximated by $V_{1i,2f}=\sum(M_l)^{-1}\langle\chi_{1i}|\hat{\mathbf{P}}_l\cdot\langle\phi_1|\hat{\mathbf{P}}_l|\phi_2\rangle|\chi_{2f}\rangle$, where l goes over all nuclei (of mass M_l) and $\hat{\mathbf{P}}_l$ are momentum operators. Equation (2) is equivalent to

$$k_{1\to2}=\int_{-\infty}^{\infty}dt\,C(t),\tag{3a}$$

$$C(t)=\sum_{ll'}(M_lM_{l'}Z_1)^{-1}\sum_i e^{-\beta E_{1i}}\langle\chi_{1i}|\hat{\mathbf{F}}_l\cdot\hat{\mathbf{P}}_l e^{iH_2t/\hbar}\hat{\mathbf{F}}_{l'}\cdot\hat{\mathbf{P}}_{l'}e^{-iH_1t/\hbar}|\chi_{1i}\rangle,\tag{3b}$$

where $\hat{\mathbf{F}}_l=\hbar^{-1}\langle\phi_1|\hat{\mathbf{P}}_l|\phi_2\rangle$ and where H_1 and H_2 are the nuclear Hamiltonians corresponding to the electronic states 1 and 2, respectively. The vector function $\mathbf{F}$ is related to the expectation values of the force acting on the nuclei by the electrons,

$$\hat{\mathbf{F}}_l=i\frac{\langle\phi_1|\partial V_{eN}/\partial R_l|\phi_2\rangle}{E_1-E_2}.\tag{4}$$

Equation (3) is the starting point for our simulations. In these simulations mixed quantum (for the electron) and classical (for the water molecules) trajectories are generated using the adiabatic simulation method [2] with the electron confined to the lowest excited state. We use the

RWK2-M (flexible) water potential and the electron-water pseudopotential derived by Barnett et al. [14]. As in our previous work [2,7(a),15], the adiabatic quantum-classical dynamics is described within the time-dependent self-consistent-field approximation. The simulations were done on a cluster of 128 water molecules with an interior excess electron which was seen [15(a)] to represent quite well the electron in bulk water. The simulation yields the classical coordinates and momenta as well as ϕ_1, ϕ_2, E_1, and E_2 (thus $\hat{\mathbf{F}}_l$) along the classical trajectory.

Our semiclassical calculation of the integrand in Eq. (3b) is based on the observation that close to the classical limit it can be approximated by

$$C(t)=\left\langle\sum_l\mathbf{F}_l^*(\mathbf{R}^{(1)}(t))\cdot\mathbf{v}_l^{(1)}(t)\mathbf{F}_l(\mathbf{R}^{(2)}(0))\cdot\mathbf{v}_l^{(2)}(0)J(t)\right\rangle_T,\tag{5a}$$

$$J(t)=\langle\chi_{1i}|e^{iH_2t/\hbar}e^{-iH_1t/\hbar}|\chi_{1i}\rangle,\tag{5b}$$

where $\mathbf{v}=\mathbf{P}/M$, $\langle\rangle_T$ denotes thermal average, and $\mathbf{R}^{(\alpha)}(t)$ and $\mathbf{v}^{(\alpha)}(t)$ $(\alpha=1,2)$ are classical positions and velocities evaluated on the electronic surfaces α, starting from initial positions and velocities associated with χ_{1i}. For the latter we take a product over the classical atoms of frozen Gaussians [16] whose time evolution follows the classical trajectory. Defining

$$G_l^{(\alpha)}(\mathbf{R}_l,t)=(a_l/\pi)^{3/4}\exp\{-\tfrac{1}{2}a_l|\mathbf{R}_l-\mathbf{R}_l^{(\alpha)}(t)|^2+(i/\hbar)\mathbf{P}_l^{(\alpha)}(t)\cdot[\mathbf{R}_l-\mathbf{R}_l^{(\alpha)}(t)]\},\tag{6}$$

we have in this approximation [16]

$$e^{-iH_\alpha t/\hbar}|\chi_{1i}\rangle=\prod_l G_l^{(\alpha)}(\mathbf{R}_l,t)\exp\left[\frac{i}{\hbar}\int_0^t L_\alpha(t')dt'\right],\tag{7}$$

where

$$L_\alpha=\sum_l[P_l^{(\alpha)}(t)]^2/M_l-\left\langle\prod_l G_l^{(\alpha)}\Big|H_\alpha\Big|\prod_l G_l^{(\alpha)}\right\rangle$$

and where the index α denotes classical propagation on the potential surface α. The choice of the parameters a_l is discussed below.

The justification for this approximation is that $J(t)$, which describes two wave packets moving on the different adiabatic surfaces and coming out of overlap, relaxes extremely fast, in times $\tau\sim15$ fs (see below). On this time scale the atoms do not move far enough to explore the anharmonicity of their local environment and a frozen-Gaussian approxi-

mation is valid. Note that the smallness of τ, resulting from the fact that many degrees of freedom contribute to (5b), is consistent with the assumed validity of the golden-rule expression.

The calculation of $k_{1\rightarrow 2}$ proceeds as follows. At ~75-fs intervals along the excited-state adiabatic trajectories we start, using the instantaneous position and momenta, adiabatic classical trajectories on the ground state, and evolve them for ~10 fs. $J(t)$ is calculated from

$$J(t) = \left\langle \prod_l G_l^{(2)}(t) \middle| \prod_l G_l^{(1)}(t) \right\rangle$$
$$\times \exp\left[\frac{i}{\hbar} \int_0^t dt' [L_1(t') - L_2(t')] \right]. \quad (8)$$

Averaging over many such short trajectories yields the thermal average, Eq. (5a).

Now consider the widths of the Gaussian packets. To eliminate the arbitrariness in their choice as much as possible we have compared the result of the present approximation to the exact evolution of the correlation function $C(t)$ for the exactly solvable case of two identical, horizontally shifted harmonic potential surfaces. The requirement that the two results are identical for short time ($\omega t \ll 1$) and high temperature ($\hbar\omega \ll kT$) leads to

$$a = 6mkT/\hbar^2 \sim (0.16\lambda_{\text{th}})^{-2}, \quad (9)$$

where $\lambda_{\text{th}} = (2\pi\hbar^2/mkT)^{1/2}$ is the thermal de Broglie wavelength. In fact, we have found that our results are almost insensitive to the choice of a for $0.01\lambda_{\text{th}} < a^{-1/2} < \lambda_{\text{th}}$ (see Fig. 2).

It is important to note certain assumptions in our method in the context of its present application. First, the validity of a classical or even a semiclassical approximation for the hydrogen atoms is not clear, though the short-time dynamics relevant to the evaluation of $k_{1\rightarrow 2}$ makes it plausible. Second, the expression (3) for $k_{1\rightarrow 2}$ is based on the assumption that the NA process proceeds from a thermal distribution of initial states. In view of the short times involved this cannot hold exactly (but possibly holds for the solvent degrees of freedom closest to the relaxing electron because of their shorter [7] adiabatic relaxation time). Finally, in the calculations reported below we have taken into account only the lowest of the three excited p-like states of the solvated electron. Since the higher p states are expected to relax more slowly (in view of the larger electronic energy gap), the relaxation time reported below may be a lower bound.

In the present calculation we have made one more approximation (which may be relaxed at the cost of a somewhat bigger computation); using the fact that $J(t)$ decays very fast, we replace Eq. (5a) by $C(t) = \sum_l \langle [\mathbf{F}_l(R(0)) \cdot \mathbf{v}_l(0)]^2 \rangle_T \langle J(t) \rangle_T$. This amounts to the Condon approximation, expressing vibronic coupling by a product of a Franck-Condon factor $\langle J(t) \rangle$ and an electronic-nuclear term $\langle (\mathbf{F} \cdot \mathbf{v})^2 \rangle$. Calculations which avoid
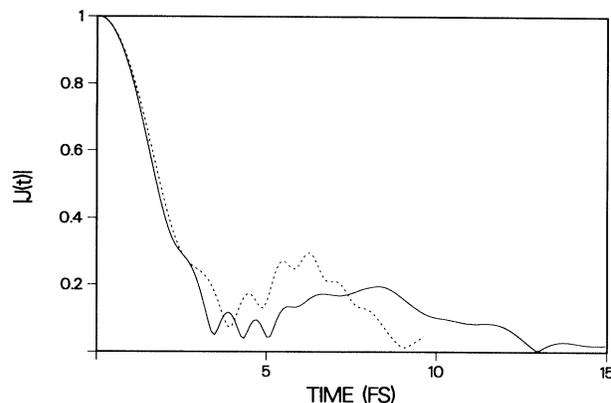
FIG. 1. The correlation function $J(t)$, Eq. (8), averaged over initial nuclear positions and momenta, for H_2O (solid line) and D_2O (dashed line). The widths used here are $\lambda = a^{-1/2} = 0.16\lambda_{\text{th}}$.

this approximation are currently underway.

Figure 1 shows the correlation function $J(t)$ for the electron in H_2O and D_2O at 300 K. These results are averages over fifteen trajectories, using the same initial conditions (with scaled velocities) for the H_2O and D_2O simulations. $J(t)$ practically vanishes at $t \cong 15$ fs, and shows only a small isotope effect. The resulting rate, however, shows a bigger isotope effect due to the nuclear velocities in the $\langle \mathbf{F} \cdot \mathbf{v} \rangle$ terms. Figure 2 shows the nonadiabatic rate $k_{1\rightarrow 2}$ as a function of the frozen-Gaussian width λ. The insensitivity of the results to this width, for $\lambda/\lambda_{\text{th}} < 1$, indicates that the proposed semiclassical evaluation of Eq. (2) is reliable.

Because of the small number of trajectories used in these first calculations, the absolute values for the rates in Fig. 2 (~120 fs for H_2O and 220 fs for D_2O) indicate only order of magnitudes, with error margins estimated at 30%-40%. Still, comparing these rates with those obtained from adiabatic simulations of electron solvation in
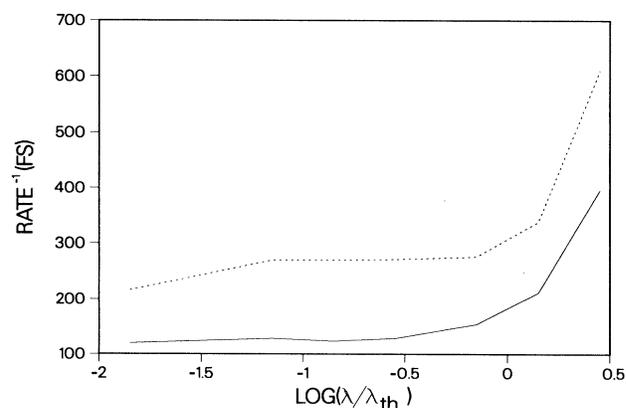
FIG. 2. The nonadiabatic rate for the transition from first-excited state to ground state of the electron in H_2O (solid line) and D_2O (dashed line), as a function of $\log_{10}(\lambda/\lambda_{\text{th}})$.

water [7] indicates that this NA relaxation of the lowest excited p-like states may be the rate-determining step in the formation of the fully solvated electron, supporting the identification of these state(s) as e_{wet} of Eq. (1). The relaxation times from Fig. 2 are shorter than those observed in Refs. [3(a)] and [4(b)] which are themselves conflicting (240 and 540 fs, respectively). The reason for this may be our use of the Condon approximation and the fact that we considered only the lowest excited p-like state. Of more concern is the relatively big isotope effect (~ 1.8) found in our simulations which is larger than that seen experimentally (1.1 and 1.4 in Refs. [3(c)] and [4(a)], respectively). More work is needed in order to determine whether these discrepancies result from our statistical errors or from deficiencies in the electron-water interaction pseudopotential (which was determined [14] by fitting with quantum chemistry calculations in the ground state but is used here to run trajectories on the excited-state potential surface).

In summary, we have presented a new semiclassical simulation method for calculating nonadiabatic transition rates in condensed phases using a mixed quantum-semiclassical representation of the electron-nuclear system, and within second order in the NA coupling. The method is useful particularly when other methods either fail or are very inefficient—in situations where the transitions are not dominated by near-crossing events. Application to the electron-water system indicates that the NA solvation process is indeed much slower than the adiabatic one, and will therefore be rate determining, thus supporting the two-state solvation picture suggested by the experimental results [3,4] and by recent theoretical calculations [8].

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