Nonadiabatic molecular dynamics simulation of photoexcitation experiments for the solvated electron in methanol

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Nonadiabatic quantum molecular dynamics simulations have been performed to simulate the pump-and-probe photoexcitation experiments of the ground state equilibrium solvated electron in methanol carried out by Barbara *et al.* [Chem. Phys. Lett. **232**, 135 (1995)]. We have characterized both the time evolution of the quantum solute, the solvated electron, and the solvation response of the classical methanol bath. The quantum energy gap provides an excellent tool to gain insight into the underlying microscopic details of the solvation process. The solvent response is characterized for both processes by a fast Gaussian component and a biexponential decay. The present results suggest that the residence time of the solvated electron in the first excited state is substantially longer than inferred from the cited experiments. The experimentally observed fast exponential portion of the relaxation more likely corresponds to the adiabatic solvent response than to the lifetime of the excited state electron. By comparing to photoexcitation simulations in water, it is shown that the simulated excited state lifetime is about three times longer in methanol than in water, predicting a less substantial increase than a recent calculation based on nonadiabatic coupling elements alone. Hydrogen-bonding statistical analysis provides interesting additional details about the dynamics. We find that the hydrogen-bonding network is significantly different in the first solvent shell around the electron in ground and first excited states, the distribution around the latter, larger and more diffuse, ion resembling more that of the pure liquid. Transformation of the corresponding hydrogen bonding structures takes place on a 1 ps time scale. © *1999 American Institute of Physics.* [S0021-9606(99)51922-3]

I. INTRODUCTION

Since its discovery[1] and later identification,[2] the solvated electron has been the subject of continuous studies by the scientific community. During these years, the curiosity of experimentalists has focused on numerous aspects of excess electrons in liquids, starting from structure, steady-state optical absorption spectroscopy, and more recently emphasizing different dynamical properties.[3–26] Although there are interesting alternative theoretical approaches to explain the properties of the equilibrium solvated electrons,[27–29] the localized cavity model has become widely accepted. Among others, molecular dynamics simulation studies based on a fully molecular model lead to a description of the solvated electron as a single entity sitting in a solvent trap and are also successful in reproducing a series of experimental observations on solvated electrons in water.[30–36] A more recent infrared spectroscopy study on negatively charged water clusters (hydrated electron clusters) and subsequent high level *ab initio* calculations are also consistent with this picture.[37–39] Similarly, density functional calculations on methanol cluster anions indicate that even relatively small clusters of polar molecules are able to localize an excess electron in a well-defined spatial region surrounded by properly oriented solvent molecules.[40]

The mechanistic question of considerable recent interest has asked how the electron initially localizes and how this state relaxes. Schematically, the ionization of a neat polar liquid leads to high energy delocalized electrons which, by continuously losing energy, first localize in a solvent void and consequently relax both electronically and configurationally. While excess electron creation in neat liquids, starting from multiphoton ionization,[22–24] is a complex issue, electron solvation represents a fairly simple element of the process where the microscopic details of solvent–solute interactions can be investigated. As such, the solvated electron system may provide uncluttered understanding of important aspects of the physics of solvent phase chemical reactions.

The last 10 years has seen tremendous improvement in both experimental and theoretical techniques applicable to this example. The availability of short laser pulses with time resolution of 100 fs or shorter enabled detailed investigations of the dynamics of the solvated electron well into the subpicosecond regime. The pump-and-probe technique made it possible to obtain reasonably good resolution transient spectra even in the fastest solvent, water.[15–21] The theoretical methods and approaches of the nonadiabatic chemical processes have experienced a similarly rapid development. Nonadiabatic molecular dynamics techniques treating the solute quantum mechanically, while describing the bath classically, are now widely employed for nonadiabatic con-

densed phase processes.[41–46] Since nonadiabatic molecular dynamics techniques can be readily implemented for the electron–classical solvent system, electron solvation has become a particularly important test of the nonadiabatic methods. A series of simulations on the hydrated electron proved to be extremely useful, for example, in developing a detailed picture of the mechanistic steps for electron solvation in water.[30–36]

The quest for a complete understanding of electron solvation is not over. Experimental work of the last few years on excess electrons in methanol has again brought up several relevant questions.[12–14] Pulse radiolysis experiments on excess electrons in methanol were among the first studies on electron solvation.[3–6,9–11] Since the early days, intense debate has continued about the possible mechanisms of the solvation dynamics of photoinduced electrons. The picture emerging from early experiments, a simple two-step model,[9,13] involving thermalization followed by solvent relaxation in the ground state, was challenged by other works.[10–12,14] One of these is a multiphoton ionization study of neat methanol at room temperature by Pépin et al. employing a pump–probe laser technique.[12] The developed hybrid model includes a continuous blueshifting mechanism in combination with a state-to-state electronic relaxation step. Based on the same set of experimental data, a subsequent numerical analysis has indicated that an alternative mechanism, proposed originally for electron hydration[32] comprising thermalization prior to a branching between localization in ground and first excited states, is equally consistent with experiment.[47] The solvation problem was illuminated from a different side by the three-pulse femtosecond laser experiments (transient hole burning) of Barbara et al.[14] They have proposed that after excitation of an equilibrium ground state electron to its first excited state, the relaxation takes place via a rapid, nonradiative electronic transition to the ground state on a time scale comparable to water, followed by a relatively long (order of 10 ps) blueshift associated with ground state solvent relaxation. Analysis of alternative, photoionization, data[13] has identified a similar longer time scale spectroscopic response with an excited state lifetime rather than with ground state solvation.

Recently a number of adiabatic molecular dynamics simulations have been performed on the excess electron in the methanol system.[48–53] In particular, Turi et al. have characterized the structure, spectroscopy, and dynamics of the solvated equilibrium electron in methanol.[49] The solvated equilibrium electron is localized in a roughly spherical ground electronic state of 2.5 Å radius surrounded by six or seven methanol molecules in the first solvent shell. The simulation reproduced the ground state optical absorption spectrum of the solvated electron reasonably well. Molecular details of the simulations pointed to the crucial role of solvent fluctuations. Further inspection revealed that while both rotational and translational motions of the solvent strongly influence the fluctuations of the individual energy levels of the solvated electron, primarily translational motions determine the fluctuations of the energy gap and, thus, also the shape of the optical absorption spectrum.[50] We have also demonstrated via adiabatic ground state simulations of non-

equilibrium relaxation following electron creation in initially neat methanol and electron annihilation in equilibrium ground state solvated electron system that, in this case, the linear response (LR) theory breaks down seriously.[51] A recent adiabatic simulation study on the photoexcitation experiment resulted in a different, nonetheless not conflicting conclusion, predicting that linear response holds well for solvation dynamics following photoexcitation.[52] Based on analysis of nonadiabatic couplings in the excited state and on the earlier analysis of solvation dynamics, it was also concluded that the nonadiabatic transition from the excited to the ground state takes place on a 10 ps time scale.[52,53]

The purpose of the present paper is to gain insight into the molecular details of the dynamics of electron solvation in methanol and to test the implications of earlier simplified analysis.[52,53] To this end, we consider nonadiabatic quantum molecular dynamics simulation of an excess electron in methanol. In particular, we simulate the three-pulse ultrafast photoexcitation experiment of Barbara et al.[14] Our first goal is, thus, to compare theory and experiment, and directly elucidate the molecular mechanism responsible for the experimental observations. Second, we compare the results of nonadiabatic simulations to the predictions based on adiabatic models, including the applicability of linear response theory for solvation dynamics and the time scales of the individual events in relaxation. We also relate the present results to those obtained for the similar problem in water both in experiment and simulation.

In Sec. II we introduce the details and procedures of our simulation model. Section III contains the primary numerical results of the present work, a qualitative characterization of the nonadiabatic trajectories (Sec. III A), and the microscopic details of electron solvation and solvation dynamics (Sec. III B). The lifetime of the excited state solvated electron and the time evolution of the hydrogen-bonding network are investigated in Secs. III C and III D. Section IV concludes the study.

II. METHODS

In the present work we perform nonadiabatic molecular dynamics computer simulations on an excess electron in methanol to model the photoexcitation experiments of Barbara et al.[14] Although the calculations are similar to those for the photoexcitation of the hydrated ground state electron,[33] obvious differences in the applied models require at least a brief review of the methodology.

We carried out molecular dynamics simulations in the microcanonical (NVE) ensemble for an excess electron placed in liquid methanol at 298 K, employing standard periodic conditions and the minimum image convention.[54] The complexity of the investigated system excludes the possibility of a fully quantum mechanical treatment. Accordingly, the solvent bath is treated classically, while the excess electron is regarded separately as a quantum mechanical object.

The methanol bath consists of 200 flexible methanol molecules in a cubic simulation box of 23.82 Å length (corresponding to the experimental neat solvent density of 0.787 g/ml at 298 K). The interactions between the methanol molecules are prescribed by the H1 intermolecular potential of

Haughney *et al.*[55] To allow for intramolecular motions of the solvent molecules we have added the intramolecular potential of Pálinkás *et al.*[56] to the intermolecular potential. The interaction between the excess electron and the methanol molecules is described by the modified pseudopotential of Zhu and Cukier.[48,49,57] The pseudopotential is expressed as a sum of four major contributions: a simple electrostatic potential between the partial charges of the methanol molecules and the electron, a polarization contribution due to the influence of the excess electron on the electron cloud of the solvent molecules, a repulsion term originating from the orthogonality requirement of the Pauli principle, and an exchange interaction term. The evaluation of all interactions (including solvent–solute interactions) is performed with a spherical cutoff centered on the oxygen site smoothed by a tapering function from 9.5 Å to the final cutoff distance of 10 Å, equivalent to that used in other works.[31–35,49–53] We note that the use of a simulation without charge compensation, as is conventional for ordinary ionic solutions, is consistent with investigation of a highly dilute system of localized charges.

In the present work, we employ the nonadiabatic dynamics algorithm developed by Webster *et al.*[46] The method combines a stochastic surface hopping algorithm[58] with the nonadiabatic scattering theory of Pechukas,[59] providing a mixed quantum-classical dynamics formalism which conserves energy without the need of *a posteriori* velocity rescaling. Since the electrons are not constrained to remain on a single electronic surface in our nonadiabatic model, state-to-state transitions between potential surfaces are possible as a consequence of the breakdown of the Born–Oppenheimer approximation. The time evolution of the solvent molecules is governed by a force which is a sum of a classical force from the solvent molecules and a quantum force originating from the quantum particle. Evaluation of the quantum force is the most important feature of the applied molecular dynamics algorithm leading to an iterative procedure within the simulation time step which takes the possibility of nonadiabatic transitions into explicit account.[46] The adiabatic spectrum at a given solvent configuration is evaluated on a 16^3 grid in a plane-wave representation using an efficient iterative and block Lanczos procedure.[46] The integration of the equations of motion is performed using the Verlet algorithm[60] for the solvent with 1 fs time step.

Although recent studies have illustrated the significance of electronic coherence loss,[61–63] in the present study we choose to drop coherence at the end of every time step. The assumption behind our choice is similar to that in hydrated electron simulations, namely, that quantum coherence decays on the time scale of the classical dynamics time steps.[30,31,33] In subsequent work, we will explore the coherence issue and its effect on the predicted dynamical properties.

The calculations here were carried out in the following way. First, we placed a free electron into an equilibrium classical solvent bath. After a 30 ps period of relaxation and equilibration of the system, the equilibrium trajectory for the ground state solvated electron was followed for an approximately 40 ps long period. We selected 15 configurations from the equilibrium trajectory with at least 2.5 ps between
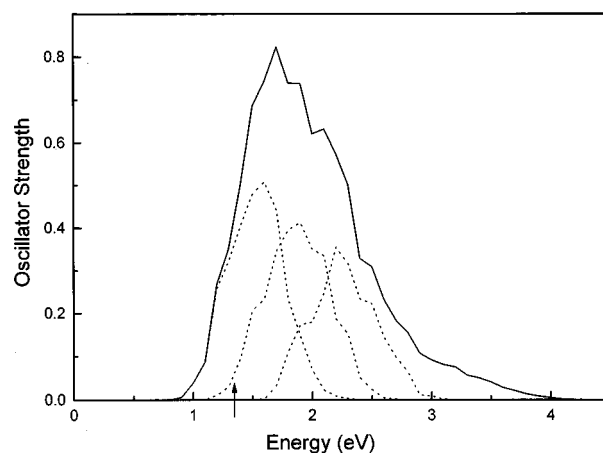

FIG. 1. Equilibrium absorption spectrum (solid line) of the ground state solvated electron in methanol. The individual subbands of three $s-p$ transitions are indicated by dotted lines. The excitation energy of the simulation of the photoexcitation experiment is shown by the arrow.

consecutive configurations according to the following criterion. Applying a linear shift of 0.25 eV to the simulated energy gaps, analogous to earlier work,[49,64] the energy gap between the ground state and the first or second excited state in the selected simulated configurations (1.34 ± 0.01 eV) is then resonant with the energy of the *experimental* pump laser (780 nm).[5] Figure 1 shows the simulated optical absorption band for the solvated ground state electron in methanol with the corresponding subbands of the first three possible transitions.[49] As can be inferred from the intensities of the first and second optical subbands of the spectrum, at the resonant energy, the pump laser can excite the ground state electron directly to the second excited state, as well. To account for this possibility, in three of the 15 chosen trajectories, the second excited state is resonant with the pump laser. In the next step, the electron was placed in the corresponding excited electronic state in the selected configuration, and the following nonequilibrium nonadiabatic dynamics were followed for a minimum of 5 ps for each trajectory.

III. RESULTS AND DISCUSSION

The following sections report the primary features of the present study. First, we examine the time evolution of the nonadiabatic trajectories. The results will be placed in the context of earlier nonadiabatic simulations for electron hydration. We will also gain insight into the macroscopically observable kinetics by focusing on ensemble averages from the 15 nonadiabatic trajectories. Comparison between experiment and theory will also be performed in terms of the photoexcitation experiments of Barbara *et al.*[14] The microscopic details of the solvation including the relaxation of the solvent and the hydrogen-bonding network will be examined at the end of the section.

A. Time evolution of the individual trajectories

Figures 2–4 show three characteristic nonadiabatic trajectories for the photoexcited solvated electron in methanol. Negative times belong to the last equilibrium portions of the
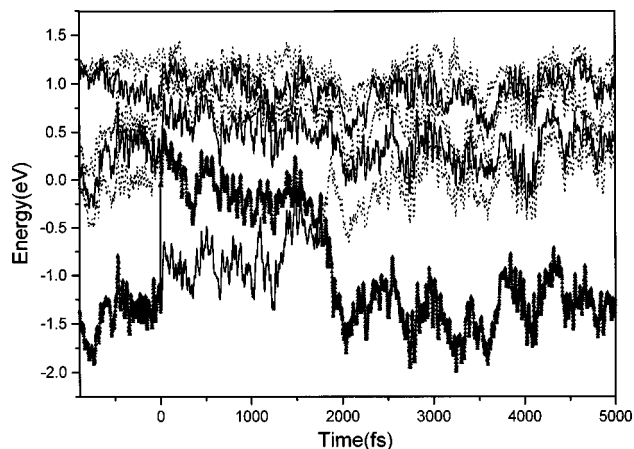
FIG. 2. Time evolution of the eigenvalues of the solvated electron eigenstates (alternating solid and dashed lines) for a typical photoexcitation trajectory. The occupied state is illustrated by the triangles. Note that the electron is promoted to the first excited state at $t=0$.

FIG. 4. Time evolution of the eigenvalues of the solvated electron eigenstates for a typical photoexcitation trajectory in which the electron is promoted to the second excited state at $t=0$. Symbols are the same as in Fig. 2.

ground state before photoexcitation takes place. At $t=0$ fs the laser pump instantaneously excites the ground state electron into its first (Figs. 2 and 3) or second excited state (Fig. 4), followed by the nonadiabatic dynamics.

The starting points of the nonadiabatic trajectories manifest the characteristic features of the ground state solvated electron. The ground state having more-or-less well-defined spherical symmetry[49] is well separated from three quasidegenerate p states. Of all the states besides the ground state, for the model used, only the first excited state spends a significant amount of time in the bound region of the energy spectrum relative to the vacuum level, while the other two p states are of slightly positive energy. We should note that an unbound state (such as the second or the third p state) is not necessarily a delocalized or continuum state as was illustrated for an excess electron in pure water configurations.[36] Moreover, a previous simulation indicated the ground state and the first three excited states of the solvated electron in methanol appear to be localized with a radius of gyration

between 2.4 and 3.8 Å.[49] The higher lying states of indefinite symmetry are well above the vacuum level and were found to be delocalized.[49] Although the bottom of the conduction band and also the vertical excitation energies are likely inaccurate in the present model, this problem could likely be remedied by explicitly including solvent polarizability. In the present study we do not use these continuum states; they are shown only for completeness. The presence of substantial energy level fluctuations is evident in the figures, and originates from the solvent fluctuations. When the electron is in its ground state, all electronic states show similar patterns, fluctuating largely in parallel.

At $t=0$, the electron is promoted to one of its excited states, resonant with the energy of the pump laser. The instantaneously altered electron distribution then perturbs the configuration of the solvent, previously equilibrated to the ground state electron. The solvent response, seen earlier for water,[33] consists mainly of solvent diffusion away from the center of mass along the long axis and into the nodal region of the newly formed p-type electronic wave function, resulting in significant changes in the energetics of the system. Although the energy of the occupied excited state does not relax significantly in half of the examined cases, the change of the unoccupied states is dramatic, a result of the fact that the excitation is vertical in the solvent coordinates. The details of the following solvent relaxation, described briefly just above, have been discussed for the corresponding case of the hydrated electron elsewhere.[33] As in the aqueous case, the energy of the unoccupied ground state initially rises sharply, then takes on a slower increase. Thus, at first glance, one can predict at least two time scales for the relaxation of the energy gap $E_1 - E_0$. We shall examine this issue in more detail in the next sections. The unoccupied states above the occupied excited state also undergo a rapid increase in energy, thus breaking the quasidegeneracy of the p states. Similarity of the polar nature of the solvent molecules in methanol and water provides a reasonable explanation for the qualitative similarity of the observed behavior of the individual energy eigenvalues in the two solvents.[33]

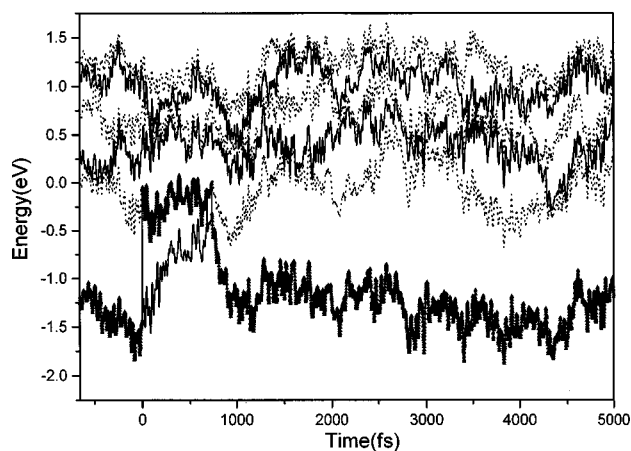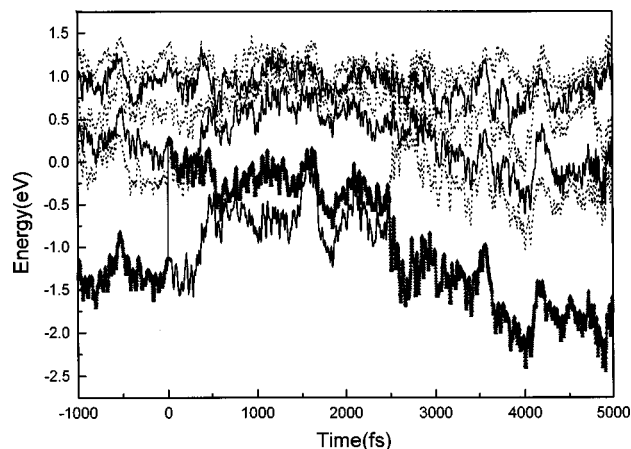Figure 2 shows a typical trajectory with relatively slow

FIG. 3. Time evolution of the eigenvalues of the solvated electron eigenstates for a less typical photoexcitation trajectory. Note the relatively short lifetime of the excited state and the very fast downward-upward-downward transition sequence at about 700 fs. Symbols are the same as in Fig. 2.

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relaxation of the occupied first excited state, slow rise of the ground state, and sharper rise of the second and third (unoccupied) excited state eigenvalues. The nonadiabatic transition takes place 1830 fs after the photoexcitation when the energy gap has decreased to about 0.2 eV. Once the electron undergoes radiationless transition, the occupied ground state energy drops initially very quickly and then more slowly, indicating the solvent response to the perturbation caused by the newly formed ground state solute. Simultaneously the unoccupied p state moves up to join the other two unoccupied p states leading to a sharp increase of the energy gap between the ground and first excited state energy levels. A less typical trajectory is shown in Fig. 3. The energy gap relaxation is very efficient, and after 690 fs radiationless transition occurs and places the electron into the ground state. The electron, however, staying only 1 fs in the ground state is promoted back to the first excited state, where it stays 50 fs more until it relaxes to the ground state for good. In another trajectory, there is a somewhat longer (10 fs) transient period after which the electron jumps back again to the excited state. A third type of trajectory is shown in Fig. 4 with the electron promoted into its second excited state. The initial radiationless transition from the second to the first excited state takes place very rapidly, less than 270 fs after the excitation. The subsequent nonadiabatic relaxation to the ground state is about an order of magnitude longer process, being completed in an additional 2.2 ps. It is immediately apparent that the excited state residence times seen here in methanol are much longer than those observed via similar methods for the aqueous case (average 730 fs).[33] We consider this question more quantitatively in Sec. III B.

B. Nonadiabatic transitions, quantum energy gap, and the solvation dynamics

We saw the general behavior of the time evolution of the individual energy levels of the solvated electron in Sec. III A. In the following we examine the connection between the time evolution of the quantum energy gap and the propensity of the excess electron to make radiationless nonadiabatic transitions. The issue has more general implications in critically evaluating the impact of solvation dynamics on excited state relaxation. Next we elaborate the question in a more quantitative manner in terms of equilibrium and nonequilibrium response functions, and the LR theory.

Figure 5 shows the ensemble averaged time evolution of the quantum energy gap between the ground state and the first excited state of the solvated electron in methanol following excitation and radiationless transition. The solid line illustrates the photoexcitation event taking place at $t=0$. Negative times correspond to the energy gap for the equilibrium ground state electron, whereas at positive times the electron stays in its first excited state. Note that ensemble averaging for excited state relaxation tends to give poorer statistics at larger times, since the survival times are different for different trajectories, and one eventually drops those trajectories from the statistics where the electron relaxes back to the ground state. The transition occurs at $\Delta E = 1.34$ eV. The energy gap dramatically decreases in the first few tens of femtoseconds and then takes on a decrease of slower pace.
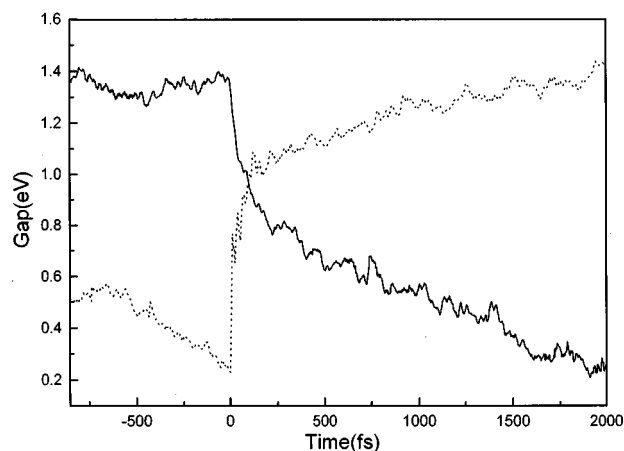

FIG. 5. Ensemble averaged dynamical evolution of the quantum energy gap between the ground and the first excited states. Solid line: electron initially in ground state; $t=0$ defined at the photoexcitation event. Dashed line: initial first excited state; $t=0$ at the radiationless transition to the ground state.

Due to this slower decay, it is only after 1.5 ps when the energy gap begins to approach its equilibrium value, 0.24 eV.[52] Although the quantum energy gap relaxes much slower in methanol than in water, the Stokes shift remains enormous, corresponding to more than 80% of the initial excitation energy. The dashed line in Fig. 5 provides information on the relaxation of the energy gap after the radiationless transition takes the electron back to the ground state. We place $t=0$ at the time step where the nonadiabatic transition occurs. Negative times, thus, correspond to the excited state electron, while positive times belong to the solvated electron once more in its ground state. One can easily see that the average energy gap where the electronic transition takes place is about 0.23 eV for the present model, less than for the model aqueous electron.[33] The ensemble averaged energy gap at the transition agrees with the equilibrium gap of 0.24 eV with the electron in the first excited state.[52] This agreement suggests that, on average, the excited state solvation is complete by the time the electronic relaxation occurs. We consider this issue further below. After the radiationless transition the solvent adjusts to the new electronic distribution of the ground state. The effect is clearly manifest in the dramatic increase of the quantum energy gap at the outset. Due to the moderate rise of the gap after the first hundred fs, the equilibrium energy gap of 1.49 eV is only slowly approached after 2 ps.

It is particularly noteworthy that the ensemble averaged energy gap evolutions shown in Fig. 5 are equivalent (after normalization) to the nonequilibrium response functions of the solvent. Nevertheless separate examination of the response functions proves to be instructive especially in terms of the LR approximation. LR states that small perturbations from equilibrium should decay in the same manner as equilibrium fluctuations do. Mathematical formulation of the linear response theory connects the equilibrium solvent response function with the nonequilibrium response function stating their equivalence[65,66]
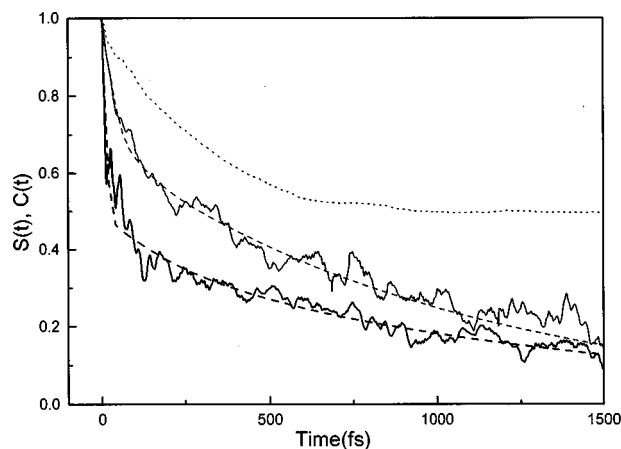
$$C(t) = S(t). \tag{1}$$

FIG. 6. Nonequilibrium solvent response functions following the upward (upper solid line) and the downward transitions (bold line) of the solvated electron in methanol. The fits to the nonequilibrium response functions are shown by dashed lines. The equilibrium energy gap autocorrelation function for the up transition is shown by dotted line (see Refs. 49 & 52).

In the context of the present study, the equilibrium response function $C(t)$ characterizes the equilibrium solvent dynamics and its effect on the quantum energy gap of the solvated electron

$$C(t) = \frac{\langle \delta\Delta E(0)\,\delta\Delta E(t)\rangle}{\langle \delta\Delta E^2\rangle}, \tag{2}$$

where $\delta\Delta E(t) = (\Delta E(t) - \langle\Delta E\rangle)$ represents the deviation of the quantum energy gap at time t from its equilibrium average value. Thus, the equilibrium response function is a time-correlation function of the fluctuations of the quantum energy gap. The corresponding nonequilibrium response function is expressed in terms of nonequilibrium averages of the quantum energy gap indicated by the overbar

$$S(t) = \frac{\overline{\Delta E(t)} - \overline{\Delta E(\infty)}}{\overline{\Delta E(0)} - \overline{\Delta E(\infty)}}. \tag{3}$$

Figure 6 shows the equilibrium solvent response function for the up transition and two different nonequilibrium response functions pertinent to the present problem, one following the upward transition of the equilibrium ground state electron and the other following the downward transition of the excited state electron. The $C(t)$ for the up transition has been calculated from a 110 ps long equilibrium ground state solvated electron trajectory.[49,50,52]

Although the $S(t)$ functions show different characteristics, especially in the first hundred fs, they possess similar qualitative features. Both functions can be described by the sum of a Gaussian and two exponentials with similar time constants (100 fs and 1 ps). We find that the biexponential part follows a much slower decay in methanol extending approximately an order of magnitude longer than in the aqueous case.[33] We have found similar dynamical features in adiabatic simulations following electron creation and annihilation in methanol.[51] We observe that the major part of the solvent relaxation is over within the first 0.3–0.5 ps. This time scale is in good accord with the experimentally ob-

served 0.5 ps fast spectral evolution.[14] Based on this observation, we suggest, similarly to an earlier equilibrium study on electron solvation in methanol,[52] that the 0.5 ps component of the experiment corresponds to the relatively fast, adiabatic response of the solvent, rather than to the lifetime of the excited state. We also note that due to the limited length of the nonadiabatic trajectories, we have not been able to observe the longer time scale solvent relaxation (7 ps time constant) suggested in Ref. 52.

The difference of the two $S(t)$ functions concentrated mainly for the first 0.5 ps (Fig. 6) is due to the ultrafast inertial part of the response. While the Gaussians decay within 10 and 30 fs for the down and up transitions, respectively, the inertial part for the down transition makes up for about half of the complete response as opposed to the less significant contribution (approximately 15%) for the up transition. The relative amplitude of the Gaussian portion is, thus, significantly smaller in methanol for the up transition than in water (38%)[33] in reasonable accord with the results predicted in classical solvation dynamics studies in methanol.[67,68] The origin of the large inertial part for the down transition is considered below.

The most significant difference, however, appears between the $C(t)$ and $S(t)$ functions for the up transition. A previous study employing adiabatic simulations of the equilibrium ground and excited state solvated electron in methanol concluded that LR theory holds well for the excitation of a ground state electron to the first excited state and the radiationless transition of an excited state electron to the ground state.[52] There, this was concluded based on the agreement between $C(t)$ functions calculated for equilibrium ground and excited states. At the same time, we have noted previously,[49] that in methanol (in contrast to water) the solvent relaxation occurs on multiple time scales which include fluctuations in the 10's of ps regime. Such slow fluctuations are necessarily challenging to sample. Hence, of the possible reasons for the difference between the corresponding equilibrium and nonequilibrium functions obtained here, we suspect that the statistical inaccuracy of the present sample of 15 trajectories may be the most important source of the unexpectedly poor agreement following photoexcitation. Nevertheless, the distinctly larger departure from the linear response result for the relaxation following the nonadiabatic transition (Fig. 6) suggests that there is, in fact, a systematic deviation between them. That this might be expected is supported by the fact that the excited state lifetime is significantly shorter than the longest time scale solvent dynamics.[52] Further support for this view comes from hydrogen bond dynamics considered below in Sec. III D.

C. Lifetime of the excited states

In the following section we estimate the lifetime of the excited state and compare the data to that obtained from experiment.[14] To this end, first we introduce the survival probability function which is calculated at time t as the ratio of the number of trajectories where the electron occupies an excited state (either first or second) to the total number of trajectories (Fig. 7). To provide a more facile discussion and motivate the understanding of the underlying details, we also
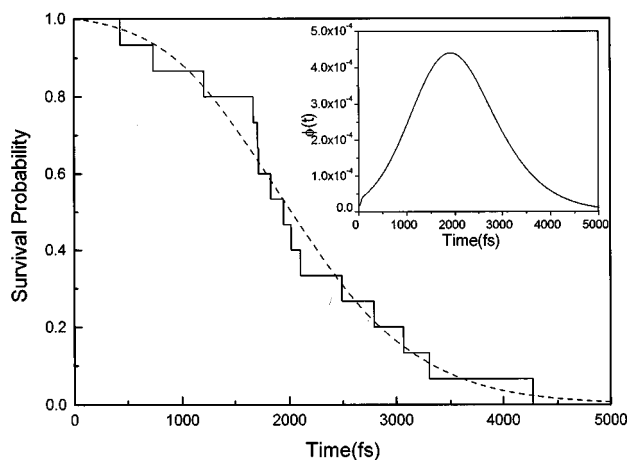
FIG. 7. Survival probability for the excited state solvated electron in methanol. The histogram represents the fraction of the trajectories where the electron occupies an excited state. The fitted dashed line is a result of a nonlinear parameter estimation procedure. The inset shows the corresponding transition density $[\phi(t)]$ for the downward transition.

introduce the transition density $\phi(t)$ shown in the inset in Fig. 7. The transition density (or transition rate) is the time derivative of the negative of the survival probability function.

Figure 7 illustrates the survival probability of the excited state electron for the trajectories of the present study. The dashed line in Fig. 7 shows a numerical fit of a nonlinear parameter estimation procedure (see below) to the histogram of the survival probability. The statistical representation of the data is similar to that for the aqueous excited state electron in Ref. 33. The number of discrete steps in Fig. 7 equals 15, the number of trajectories run in the present simulation. The excited state lifetimes span a wide range between 434 and 4271 fs. Similarly to the qualitative shape for the water case,[33] the survival probability decreases slowly at short times ($t < 500$ fs) with a negative curvature up to the inflexion at about 2 ps, and decays exponentially at longer times. Correspondingly, the transition density has a maximum at the inflexion of the original distribution function and decreases monotonically to zero at larger times (see the inset in Fig. 7). It is interesting to note that more than half of these transitions occur between 1600 and 2100 fs. The average lifetime of the excited state is about 2050 fs computed from the transition density, approximately three times the corresponding value for the model of the excited state aqueous electron.[33] Significantly longer excited state lifetime is predicted in methanol from adiabatic simulations comparing only the nonadiabatic coupling matrix elements connecting the two states for water and methanol.[53]

To estimate the lifetime of the equilibrium excited state electron one needs a functional relation between the transition density, the population of the excited state, and the time-dependent energy gap. In the following *ad hoc* model we assume first order kinetics with the transition density proportional to the population of the excited state. Inversely proportional dependence of the transition density on the quantum energy gap, found to apply for water,[33] gives poor agreement with the simulated data here. Hence we propose

the following differential equation employing a simple series expansion in the gap $U(t)$ up to the third power:

$$\frac{dP(t)}{dt} = \frac{-P(t)}{\tau_1 U(t) + \tau_2 U(t)^2 + \tau_3 U(t)^3}, \tag{4}$$

where $U(t)$ is taken from the fit to the time evolution of the ensemble average of the quantum energy gap following photoexcitation (Fig. 5), normalized to the equilibrium value of the energy gap. We employed numerical integration of Eq. (4) in a nonlinear parameter estimation procedure to fit the simulated survival probability data. We note that Eq. (4) allows for a stronger dependence of the transition rate on the quantum energy gap for methanol with significant contribution from the third-order term ($\tau_1 = 320$ fs, $\tau_2 \approx 0$ fs, $\tau_3 = 340$ fs) than was observed for water.[33] The fit shown in Fig. 7 is acceptable, while the inset presents the calculated transition density. The estimated asymptotic lifetime of the equilibrium excited state electron is obtained as the sum of the three estimated parameters of Eq. (4) [as $t \to \infty$, $U(t) \to 1$, and, thus, Eq. (4) simplifies to first-order kinetics]. Thus, the equilibrium nonradiative excited state lifetime after the gap reached its equilibrium value turns out to be only about 660 fs, significantly less than the average lifetime of the excited state and comparable to the 450 fs found for water.[33] This small difference can still be considered quite sizeable considering the 2.5 times larger equilibrium gap for water than that for methanol. Had the energy gap in water been the same size as in methanol and were the transition probability for water to follow the same inversely proportional model of Ref. 33, then the corresponding excited state lifetime in methanol would exceed that in water by approximately a factor of 4 similarly to the average excited state lifetime.

The present findings are consistent with the transient hole-burning experiment of Barbara *et al.*[14] regarding at least two aspects. Comparison of the present study and experimental works[14] on excited state electron solvation in methanol to both experiments[69] and simulations[33] on photoexcited hydrated electrons predicts significantly slower dynamics in methanol than in water. Furthermore, the qualitative agreement with experiment is especially encouraging with respect to the time scale of the complete relaxation (starting from the photoexcitation through excited state dynamics and ground state dynamics). The experimentally observed 6 ps time scale[14] agrees reasonably well with the sum of the 2 ps excited state lifetime and the approximately 1 ps time scale for ground state solvation of the present study. If one considers the observation that the use of the classical flexible model of the solvent molecules, being able to accept any amount of energy from the relaxing electron, leads to significantly faster energy disposal than in a more realistic model with quantized vibrational modes,[31,33] then the agreement is even more satisfying. Significant differences, however, exist between the simulated results and the experimentally developed model for excited state solvation. The experimental work suggests a relatively short excited state lifetime (0.5 ps) followed by an order of magnitude longer ground state solvation of 5.4 ps time constant. We, on the other hand, pro-
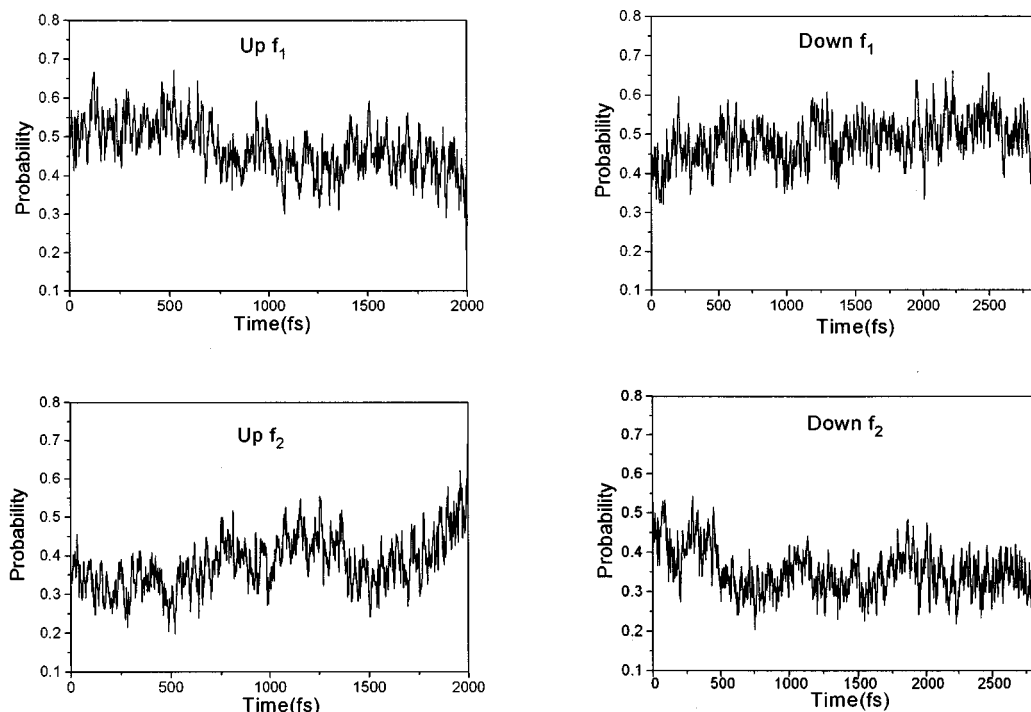
FIG. 8. Fraction of hydrogen-bonded methanol molecules in the first solvent shell around the solvated electron participating in one and two hydrogen bonds to other MeOH molecules (f_1 and f_2, respectively) for up and down transitions, as a function of time. The plots on the left side illustrate the hydrogen-bonding dynamics after photoexcitation (up transition), whereas those on the right side show the dynamics following the radiationless (down) transition.

posed in Sec. III B that the experimentally observed 0.5 ps fast spectral evolution may be explained in terms of excited state solvation dynamics.

D. Hydrogen-bonding dynamics

The experimentally observable solvation dynamics is a direct manifestation of the molecular motions. The microscopic details of the solvation dynamics following photoexcitation of a ground state equilibrium hydrated electron were thoroughly discussed previously.[33] Here we carry out a statistical analysis for the hydrogen-bonding network of the solvent. The examination of the time evolution of the hydrogen-bonding system is relevant for two reasons. First, it provides an interesting alternative route to elucidate the solvent dynamics from the perspective of the molecular interactions of the solvent. Second, the fact that the hydrogen-bonding systems of liquid water and methanol are different was invoked in comparisons of the experimentally measured time scales of electron solvation in polar liquids.[14,47] Therefore such interactions may well be informative when viewed directly.

The method we pursue here is similar to that employed in our earlier adiabatic simulation study of electron creation in methanol.[51] First, we define hydrogen bonds, using two geometric parameters. Two methanol molecules are considered to be hydrogen bonded if the corresponding O...H distance is less than 2.5 Å and the O–H...O hydrogen-bonding angle is larger than 150°. This definition proved to be effective in earlier liquid simulation studies and gave good agreement with an alternative energetic definition.[70] The unified site model of the methyl group does not allow evaluation of the significance of the possible C–H...O hydrogen-bonding

interactions.[40,70] We calculate the ensemble average of the fraction of the molecules which participate in zero, one, two, or more than two hydrogen bonds (f_0, f_1, f_2, and f_3, respectively) to other solvent molecules. The analysis is performed as a function of time. Another interesting aspect appears if one considers the different solvation shells around the solvated electron. The first solvation shell is defined to include all solvent molecules which are closer to the center of mass of the electron than 5 Å. We draw the second shell between 5 and 10 Å, and also examine the remaining part of the solvent as well. We also have to keep in mind that, since the excited state electron is not spherically symmetric, examination of the fraction of the hydrogen bonded molecules in the individual solvent shells is more informative than that of the occupation numbers.

We focus the analysis on two different initial conditions: (a) the photoexcitation event or (b) the radiationless transition. This separation is essentially similar to that illustrated in Fig. 5 for the energy gap. Figure 8 illustrates the time evolution of the hydrogen-bonding fraction of the methanol molecules. The second and third solvation shells (not shown) exhibit no particularly distinctive details, with the distribution of the hydrogen bonds roughly equivalent with that of the pure methanol liquid ($f_2 \approx 0.6$, $f_1 \approx 0.3$, $f_0 \approx 0.05$).[51,55] The patterns are substantially different for the first solvent shell. For short times after the up transition, and at large times after the down transition, the hydrogen bonding distributions approach that for the ground state equilibrium solvated electron. That is, the tendency is opposite compared to pure methanol liquid, with a significantly larger fraction of single hydrogen bonded molecules f_1 in the first coordina-

tion shell. We pointed out earlier[51] that this finding is a direct reflection of the increased number of dangling hydrogens in the first solvent shell orienting toward the negatively charged solvated electron. What is more interesting is the evolution of the hydrogen-bonding distribution between the ground state and the excited state. Following photoexcitation, the excited state electron distribution distorts the solvent cavity with associated changes in the hydrogen bonding distribution. After 2 ps, the fraction of the solvent molecules with two hydrogen bonds to other MeOH molecules almost doubles, while f_1 decreases significantly. The resulting distribution around the excited state solute resembles more that of the neat liquid than that of the ground state solute. The origin of this particular difference between the hydrogen-bonding topology around the ground state electron and the first excited state electron in the first solvent shell can be explained by the more diffuse nature of the excited state charge orienting the solvent molecules, analogous to the solvation of large classical ions. The time evolution of the hydrogen-bonding distribution following the radiationless down transition exhibits similar features, but roughly reversed in time. It takes less than 1 ps for f_1 to exceed f_2. The remaining relaxation of the hydrogen-bonding network follows more slowly, approaching the ground state distribution. We note here that the hydrogen bonding dynamics following up and down transitions show different amplitude. This also supports earlier observations that the excited state configurations may not fully sample the equilibrium distribution leading to the observed faster dynamics after nonadiabatic relaxation than following the up transition. The roughly 2 ps time scale to adjust the hydrogen-bonding network fully to the new electron distribution is common to both up and down transitions. The presence of these ps time scale changes, evident in all distributions, points to the important role hindered translation plays in solvent relaxation following photoexcitation and nonradiative transition.

IV. CONCLUSIONS

We have performed nonadiabatic quantum molecular dynamics simulations to gain insight into the microscopic details underlying recent photoexcitation experiments on solvated electrons in methanol. The solvated electron problem provides an excellent opportunity to study the coupling between the quantum states of the solute and the dielectric and mechanical response of the solvent. The time evolution of the quantum energy gap has been recognized as a sensitive tool to monitor solvent response after perturbations in similar studies.[33] In methanol, the solvent response follows somewhat different patterns following photoexcitation of the ground state electron and following radiationless transition of the excited state electron. Although we concluded that insufficient statistical accuracy probably prevents us from testing the validity of linear response as suggested in another study,[52] we found that the qualitative features of the response functions are informative. The response functions consist of a fast Gaussian inertial part and a biexponential decay. The time scale of the biexponential part is similar to the initial exponential component found in experiments.[14] The present work suggests that the original interpretation identifying this

decay with the lifetime of the excited state electron should be supplanted, and that the experimentally observed 0.5 ps fast part[14] corresponds to excited state solvent response as suggested on the basis of less direct evidence earlier.[52] We also pointed out reasonably good agreement between the experimental[14] and simulated time scales necessary for the complete relaxation of the ground state electron after photoexcitation and radiationless transition. The simulated lifetime of the solvated electron turns out to be much longer (approximately three times) than the corresponding simulated quantity for the hydrated electron.

Employing a gap dependent rate equation for the nonradiative transition rate, we estimate the lifetime for the equilibrium excited state solvated electron in methanol to be shorter by approximately a factor of 3 than the average excited state lifetime. Further, the dependence of the nonradiative transition rate on the quantum energy gap is predicted to be both stronger and more complex in methanol than in water.[33]

A novel time-dependent hydrogen-bonding analysis for the solvent molecules revealed significant differences in the hydrogen-bonding network around the ground state solute compared to the excited state solute in the first solvation sphere. The distribution around the excited state is found to resemble more closely that of the pure liquid, in accord with classical simulations of large ions. Dynamical analysis has shown that the time scales of the solvent response functions qualitatively reflect the hydrogen-bonding dynamics. The increased complexity of these dynamics in methanol compared to water demonstrates that the multiple time scales characterizing nonaqueous solvents can have important consequences for excited state dynamics.

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