A time-dependent polarizable continuum model: Theory and application

Marco Caricato, Francesca Ingrosso, Benedetta Mennucci, and Jacopo Tomasi

---

Articles you may be interested in

Comparison of the Marcus and Pekar partitions in the context of non-equilibrium, polarizable-continuum solvation models
J. Chem. Phys. **143**, 204104 (2015); 10.1063/1.4936357

Comparison of polarizable continuum model and quantum mechanics/molecular mechanics solute electronic polarization: Study of the optical and magnetic properties of diazines in water
J. Chem. Phys. **135**, 144103 (2011); 10.1063/1.3644894

Geometries and properties of excited states in the gas phase and in solution: Theory and application of a time-dependent density functional theory polarizable continuum model
J. Chem. Phys. **124**, 094107 (2006); 10.1063/1.2173258

Two-photon absorption in solution by means of time-dependent density-functional theory and the polarizable continuum model
J. Chem. Phys. **122**, 244104 (2005); 10.1063/1.1944727

Polarizable continuum model study of solvent effects on electronic circular dichroism parameters
J. Chem. Phys. **122**, 024106 (2005); 10.1063/1.1829046

A time-dependent polarizable continuum model: Theory and application

Marco Caricato[a)]
Scuola Normale Superiore, Piazza dei Cavalieri 7, 56126 Pisa, Italy

Francesca Ingrosso, Benedetta Mennucci, and Jacopo Tomasi
Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Risorgimento 35, 56126 Pisa, Italy

This work presents an extention of the polarizable continuum model to explicitly describe the time-dependent response of the solvent to a change in the solute charge distribution. Starting from an initial situation in which solute and solvent are in equilibrium, we are interested in modeling the time-dependent evolution of the solvent response, and consequently of the solute-solvent interaction, after a perturbation in this equilibrium situation has been switched on. The model introduces an explicit time-dependent treatment of the polarization by means of the linear-response theory. Two strategies are tested to account for this time dependence: the first one employs the Debye model for the dielectric relaxation, which assumes an exponential decay of the solvent polarization; the second one is based on a fitting of the experimental data of the solvent complex dielectric permittivity. The first approach is simpler and possibly less accurate but allows one to write an analytic expression of the equations. By contrast, the second approach is closer to the experimental evidence but it is limited to the availability of experimental data. The model is applied to the ionization process of *N,N*-dimethyl-aniline in both acetonitrile and water. The nonequilibrium free-energy profile is studied both as a function of the solvent relaxation coordinate and as a function of time. The solvent reorganization energy is evaluated as well. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1879952]

I. INTRODUCTION

In the modeling of time-dependent phenomena in solution, one of the open questions is how to take into account the evolution of the interaction between solute and solvent. In fast processes, such as electronic excitations, electron transfers, or ionizations, the time scale of the change in the charge density of the solute is usually much smaller than the time scale in which a polar solvent fully relaxes to reach a new equilibrium state. During this relaxation, the solvent nuclear and molecular motions act as inertia on the solvation response and a nonequilibrium regime is established. Due to the mutual solute-solvent polarization, the new equilibrium is reached through changes of both solute and solvent, and an accurate description of the reorganization path should consider the evolution of this interaction and, possibly, the solute geometry relaxation.

The most straightforward way to describe this evolution is represented by molecular-dynamics (MD) simulations of the solute-solvent system.[1–5] In this case, the time dependence of the solvent polarization is obtained explicitly from the simulated trajectories. In the methodology based on molecular-dynamics simulations, the typical way[5] to run nonequilibrium simulations is to start from equilibrated trajectories corresponding to the initial state and change the solute partial charges, according to the final-state values. Each simulation is then run and the results obtained for the solvation energy are averaged over the full set of trajectories.

An alternative approach to MD simulations is the one proposed by implicit solvation models. In these models the polarization is determined by the dielectric function ε of the solvent, described as a continuum medium in which a cavity hosts the solute. Continuum models developed to treat the time-dependent solvation response can be classified into two main classes. Models belonging to the first class introduce a separation of the solvent polarization into a dynamical contribution, associated with the electronic motion, and an inertial (or orientational) contribution, due to the nuclear and molecular motion.[6–8] Models of the second class implicitly take into account dynamical and inertial effects in a single response.[9–13] When the nonequilibrium response is described in terms of two contributions, the orientational component of the polarization remains in equilibrium with the charge density of the initial state. On the other hand, the dynamical component is assumed to equilibrate instantaneously to the final state in the presence of the inertial part of the polarization. By contrast, when a single term in the solvent response is considered,[9–13] the transition is represented as a step change in the solute charge density, and the solvent response is modeled by introducing the complex dielectric permittivity as a function of the frequency, $\hat{\varepsilon}(\omega)$.

Besides the discrete and the continuum approaches, there is a third alternative way to calculate the nonequilibrium solvation energy. In this framework, a thermodynamic cycle is defined in terms of a series of intermediate states in which solute and solvent are in equilibrium. The properties of interest are then calculated on the basis of modified-reference

[a)]Electronic mail: m.caricato@sns.it

122, 154501-1

interaction site model (RISM) methods [ex-RISM (Ref. 14) and RISM-self-consistent-field (SCF) (Refs. 15 and 16)].

The method presented here belongs to the family of continuum models and it is developed according to the strategy in which the solvent response is a global response. It is based on a continuum representation of the solvent within the polarizable continuum model[17] (PCM) approach. This model allows a realistic representation of the cavity in which the solute is embedded as well as a quantum-mechanical description of the solute, and therefore it represents a tool to accurately describe the effects of solvation on molecular phenomena and properties. In particular, the interest here is on the description of the solvent reorganization after sudden changes in the solute charge distribution.

The procedure that we propose within the PCM formalism to model the solvent relaxation differs from the nonequilibrium formulation already mentioned (see Refs. 6–8). In fact, here we adopt the strategy based on the inclusion of the complex dielectric permittivity in order to take into account the solvent motion activated as a consequence of the change in the solute. This work therefore represents a further step in the description of solute-solvent interaction in time-dependent processes, since it allows us to follow the evolution of the solvent polarization in a straightforward way and to maintain an accurate description of the solute. It is important to remark that a full inclusion of the time-dependent solute-solvent polarization would lead to an extremely complex formulation, due to nonlinear effects induced by the solvent reaction field on the solute charge distribution which can be seen as a function of such field. In the present approach, as in previous ones,[9] this complexity is avoided by assuming a linear approximation. In Sec. II E we discuss this issue more in details.

The time-dependent model is here applied to the study of the change of the solute-solvent interaction energy after an ionization process. The solute studied is N,N-dimethyl-aniline (DMA) and the solvents considered are acetonitrile and water. This choice has been dictated by the fact that it represents a simple, but still realistic, model for more complicated phenomena, such as electron transfer in solution, and it also gives us the opportunity to compare with a previous study[15] based on the same solute-solvent system.

This paper is organized as follows. In Sec. II the main formal aspects of the model are presented: after a brief introduction to the PCM formalism in Sec. II A, the time-dependent theory is extensively treated in Secs. II B–II E. Section II F is devoted to a numerical test on a simplified system: a solute represented by a nonpolarizable point charge moving along the axis of a cylindric cavity immersed in water. Section III presents and analyzes the results of the study of the ionization of DMA in water and acetonitrile. Finally, Sec. IV presents a summary with indication of some possible extensions and generalizations of the model.

II. THEORY

A. The PCM formalism

In the PCM model, the solvent is represented by a continuum dielectric medium within which a cavity is built to host the solute. The solute-solvent interaction is expressed in terms of a solvent reaction field, which is obtained, for the electrostatic polarization, solving the Poisson–Laplace equations with the proper boundary conditions.[17] This reaction field is thus represented by an apparent surface charge (ASC) placed on the surface cavity S. The numerical solution of this electrostatic problem is achieved by a boundary-element method (BEM) approach: the cavity surface is divided in small regions, called tesserae, and the ASC is rewritten in terms of pointlike charges centered on the tesserae.

In the last years, different formulations of the PCM model have been presented.[18,19] They differ in the way the PCM equations determining the ASCs are defined. Here, in particular, we shall adopt the recent iterative version of the dielectric PCM (DPCM).[20] In this case, for a solute enclosed in the molecular cavity, the solvent reaction field can be expressed in terms of the ASC $\sigma(s)$ in a point $s \varepsilon S$ as

$$\left(\frac{\varepsilon+1}{\varepsilon-1} - \frac{1}{2\pi}D^*\right)\sigma(s) = -\frac{1}{2\pi}E_\perp(s), \qquad (1)$$

where ε is the static dielectric permittivity of the solvent and D^* is an operator that accounts for the electric field generated by σ itself. $E_\perp$ is the normal component of the electric field generated by the solute on the cavity surface. As said above, the σ charge distribution is approximated in terms of the point charges located at the center of each tessera. Equation (1) is thus transformed into the expression

$$\left(2\pi\frac{\varepsilon+1}{\varepsilon-1}\mathbf{A}^{-1} - \mathbf{D}^*\right)\mathbf{q} = -\mathbf{E}_\perp. \qquad (2)$$

The **A** matrix is a diagonal matrix with the areas of the tesserae (a_i) as elements. Introducing the vectors:

$$z_i(a_j) = \sum_{j\neq i} D_{ij}a_j, \qquad (3)$$

$$z_i^*(q_j) = \sum_{j\neq i} D_{ij}^*q_j, \qquad (4)$$

the expression (2) can be rewritten as[20]

$$\left\{\frac{1}{a_i}\left(\frac{4\pi\varepsilon}{\varepsilon-1} + z_i(a_j)\right)\right\}q_i - z_i^*(q_j) = -(E_\perp)_i. \qquad (5)$$

For a definition of the matrix elements D_{ij} and D_{ij}^* we refer to the original work.[20]

Equation (5) is iteratively solved[20] setting

$$q_i^{(n)} = \left\{\frac{1}{a_i}\left(\frac{4\pi\varepsilon}{\varepsilon-1} + z_i(a_j)\right)\right\}^{-1}\left\{-(E_\perp)_i + z_i^*[q_j^{(n-1)}]\right\}. \qquad (6)$$

This particular formulation of the PCM equation is here preferred due to the direct relation between apparent charges and electric field which is well suited for a linear-response treatment of the solvation response (see Secs. II B and II D).

B. Treatment of the time evolution: The single-step change

In this section we present the basic aspects of the model used to describe the time-dependent response of the solvent

to a time evolution of the solute charge distribution, represented by a single time step. A more general case involving multiple steps will be presented in Sec. II C.

We assume that the variation in the normal component of the electric field $(E_\perp)_i$ on a tessera i from the initial to the final state is a step change of the type,

$$(E_\perp)_i(t) = (E_\perp)_i^{\text{init}} + \theta(t)(\Delta E_\perp)_i, \tag{7}$$

where the function $\theta(t)$ is the step function and

$$(\Delta E_\perp)_i = (E_\perp)_i^{\text{fin}} - (E_\perp)_i^{\text{init}}. \tag{8}$$

If the electric field acting on the solute is not subject to further changes after the step change, the time-dependent solvent polarization charges at a generic time t can be written as

$$\mathbf{q}(t) = \mathbf{q}^{\text{init}} + \delta\mathbf{q}(\Delta\mathbf{E}_\perp, t), \tag{9}$$

where $\mathbf{q}^{\text{init}}$ are the polarization charges when the initial solute-solvent equilibrium is valid $(t \to -\infty)$ and the following boundary conditions apply

$$\mathbf{q}(t \to -\infty) = \mathbf{q}^{\text{init}},$$
$$\delta\mathbf{q}(t \to -\infty) = 0, \tag{10}$$

and

$$\mathbf{q}(t \to \infty) = \mathbf{q}^{\text{fin}},$$
$$\delta\mathbf{q}(t \to \infty) = \Delta\mathbf{q} = \mathbf{q}^{\text{fin}} - \mathbf{q}^{\text{init}}. \tag{11}$$

In relations (9) and (11), the time at which the perturbation starts is $t=0$. Before the perturbation takes place $(t \to -\infty)$ the term $\delta\mathbf{q}$ is nil since $\Delta\mathbf{E}_\perp = 0$. $\mathbf{q}^{\text{fin}}$ are the polarization charges when the solute-solvent equilibrium has been reached in the final state.

Considering the solvent as a dielectric material polarized by the presence of an external electric field, under the assumption that the coupling between the field and the system is weak, it is possible to apply the results of the linear-response theory.[21] This means that the response of the system can be fully described in terms of time correlation functions characteristic of the system in the absence of perturbation. We report here the results of the theory when applied to the properties we are interested in. More details on the theory can be found in Ref. 21. The polarization P induced in a point r inside the medium at time t due to an electric field E in r at t' can be written as

$$P(r,t) = \int dr' \int_{-\infty}^{t} \chi(r-r', t-t') E(r', t') dt', \tag{12}$$

where χ represents the medium response function. The physical meaning of Eq. (12) is that the response at time t, i.e., the change in the value of the polarization, is a superimposition of delayed effects, and that the response at time t to a unit, δ function-shaped external electric field applied at $t=0$ is simply the medium response function χ.[22] In the present case, since the medium is assumed to be local, homogeneous, and isotropic, the result is a spatial average of Eq. (12). In this scheme and by analogy with the expression

of the polarization in Eq. (12), the variation of the polarization charges $\delta\mathbf{q}$ at time t can be written as a response to the change in the electric field, namely,

$$\delta\mathbf{q}(\Delta\mathbf{E}_\perp, t) = \int_{-\infty}^{t} dt' \mathbf{R}(t-t') \theta(t') \Delta\mathbf{E}_\perp. \tag{13}$$

This equation represents the time-dependent version of Eq. (2) for the field change. We can solve Eq. (13) using the iterative procedure summarized in Eq. (6) for each time t.

C. A more general case: The multistep change

When the solute charge distribution is subject to a multistep time evolution, the solvent cannot establish an equilibrium situation with the solute at each step. We therefore model the solvent response by considering the subsequent step changes in the solute electric field, occurring at $t = 0, t_1, t_2, \ldots t_n$. Before the perturbation starts, Eq. (9) applies and, between $t = t_{k-1}$ and $t = t_k$, the change in the field $\Delta\mathbf{E}_\perp^{k-1,k}$ is determined by Eq. (7). The polarization charges at different times then become

$$\mathbf{q}(t) = \mathbf{q}^{\text{init}} + \int_{-\infty}^{t} dt' \mathbf{R}(t-t') \theta(t') \Delta\mathbf{E}_\perp^{0,1}, \quad 0 \leq t < t_1,$$

$$\mathbf{q}(t) = \mathbf{q}^{\text{init}} + \int_{-\infty}^{t} dt' \mathbf{R}(t-t') \theta(t') \Delta\mathbf{E}_\perp^{0,1} + \int_{-\infty}^{t-t_1} dt' \mathbf{R}(t-t') \theta(t'-t_1) \Delta\mathbf{E}_\perp^{1,2}, \quad t_1 \leq t < t_2,$$

$$\cdots \tag{14}$$

$$\mathbf{q}(t) = \mathbf{q}^{\text{init}} + \int_{-\infty}^{t} dt' \mathbf{R}(t-t') \theta(t') \Delta\mathbf{E}_\perp^{0,1} + \cdots$$
$$+ \int_{-\infty}^{t-t_{n-1}} dt' \mathbf{R}(t-t') \theta(t'-t_{n-1}) \Delta\mathbf{E}_\perp^{n-1,n},$$
$$t_{n-1} \leq t < t_n.$$

Equation (14) can be cast in a more compact form as

$$\mathbf{q}(t) = \mathbf{q}^{\text{init}} + \delta\mathbf{q}(\Delta\mathbf{E}_\perp^{0,1}, t), \quad 0 \leq t \leq t_1,$$

$$\mathbf{q}(t) = \mathbf{q}^{\text{init}} + \delta\mathbf{q}(\Delta\mathbf{E}_\perp^{0,1}, t) + \delta\mathbf{q}(\Delta\mathbf{E}_\perp^{1,2}, t-t_1),$$
$$t_1 \leq t \leq t_2,$$

$$\cdots \tag{15}$$

$$\mathbf{q}(t) = \mathbf{q}^{\text{init}} + \delta\mathbf{q}(\Delta\mathbf{E}_\perp^{0,1}, t) + \cdots + \delta\mathbf{q}(\Delta\mathbf{E}_\perp^{n-1,n}, t-t_{n-1}), \quad t_{n-1} \leq t \leq t_n,$$

where the terms $\delta\mathbf{q}$ (except the last one) represent a sort of memory of the polarization in the preceeding steps. These terms act as inertia on the charges at $t_{m-1} \leq t < t_m$ ($2 \leq m \leq n$) and they rapidly decrease as time increases.
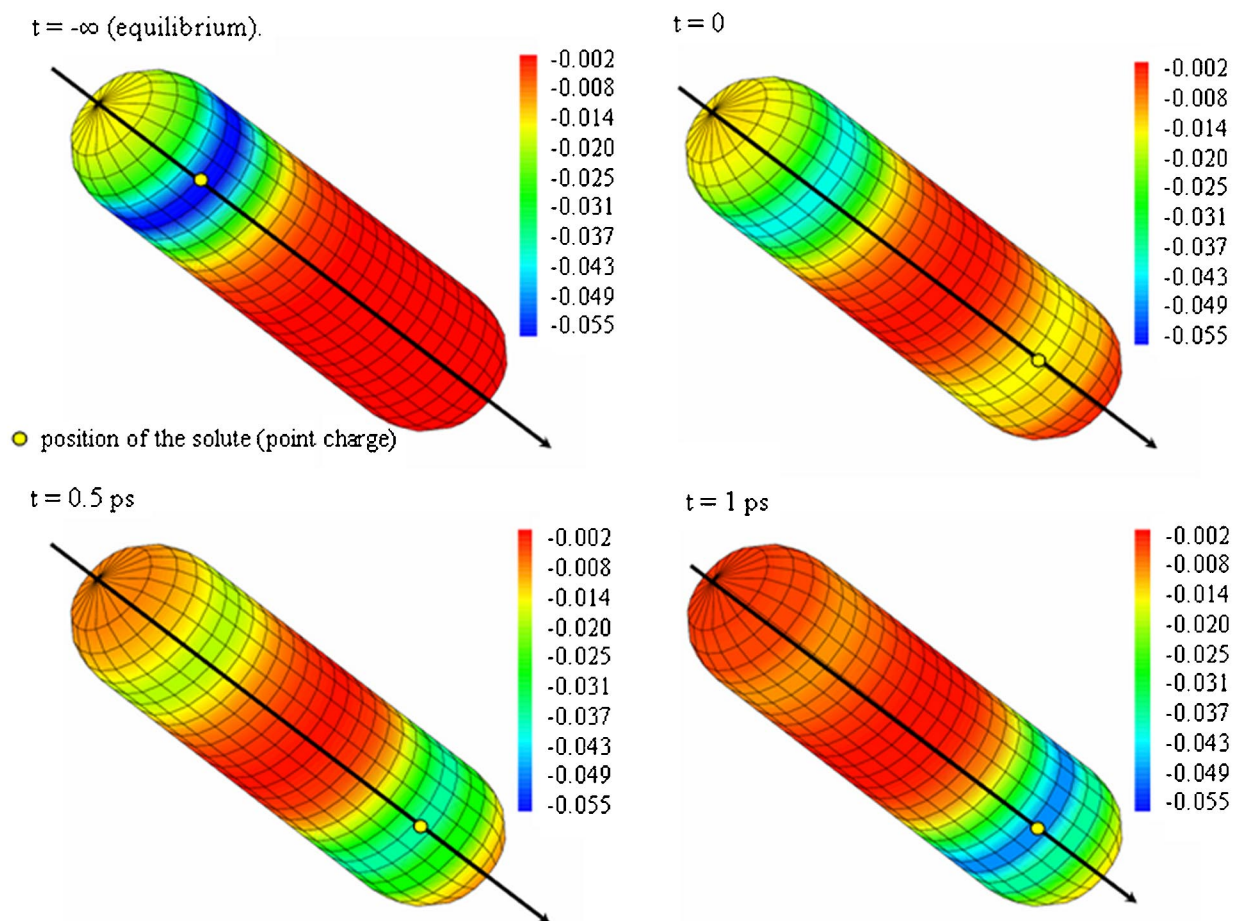
FIG. 1. Time evolution of the apparent charges located on the cavity surface after a step change in the solute position. Four main snapshots of the evolution are shown.

D. Time-dependent variation of the polarization charges

The theoretical model outlined in Sec. II B and II C is transformed in a numerical procedure by passing from the time domain to the frequency domain. This change is required as the dielectric response of the solvent is described in terms of its complex dielectric permittivity as a function of the frequency ω. The ω dependence of $\hat{\varepsilon}$ can either be modeled using pure diffusive expressions (as in the Debye relaxation expression[23]), or calculated on the basis of the experimental measurements of the absorption. The use of the Laplace-transformed equations to pass from the time to the frequency domain has the effect of simplifying the formalism and of allowing the straightforward use of the function $\hat{\varepsilon}(\omega)$.[13,24] To understand this procedure let us go back to the basic Eq. (13), defining the time evolution of the charge, and let us revert it in the iterative form. Using Eq. (13) the variation of the charge on each tessera i is expressed as

$$\delta q_i^{(n)}[(\Delta E_\perp)_i, t] = g_i(t)\left\{-(\Delta E_\perp)_i + z_i^*\left[\delta q_j^{(n-1)}\right]\right\}$$
$$- \frac{z_i[a_j]}{a_i}\delta q_i^{(n-1)},$$
(16)

where we have defined

$$g_i(t) = \int_{-\infty}^{t} dt' R_i(t-t')\theta(t').$$
(17)

By applying a procedure originally developed by Hsu *et al.*[13] and successively modified for the PCM approach,[24] the $g_i(t)$ function in Eq. (17) becomes

$$g_i(t) \simeq \frac{2}{\pi}\int_0^\infty \frac{d\omega}{\omega}Im\left[\tilde{R}_i(\omega)\right]\cos \omega t + \tilde{R}_i(0) = g_i'(t) + \tilde{R}_i(0),$$
(18)

being

$$\tilde{R}_i(0) = \left\{\frac{1}{a_i}\left[\frac{4\pi\varepsilon}{\varepsilon-1}\right]\right\}^{-1}$$
(19)

and

$$\tilde{R}_i(\omega) = \left\{\frac{1}{a_i}\left[\frac{4\pi\hat{\varepsilon}(\omega)}{\hat{\varepsilon}(\omega)-1}\right]\right\}^{-1}.$$
(20)

A simple expression for the $\hat{\varepsilon}(\omega)$ is provided by the Debye model for the solvent relaxation
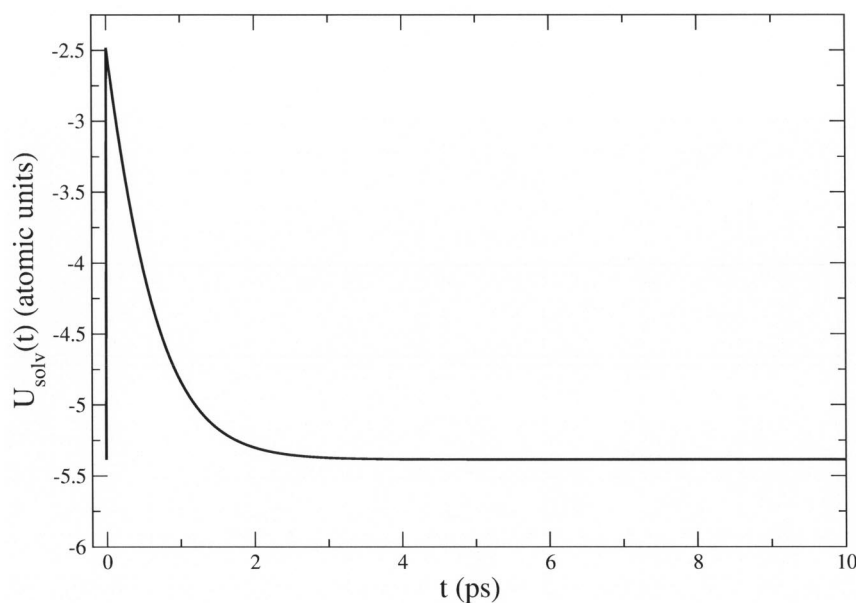
FIG. 2. Time evolution of the solute-solvent interaction energy $U_{\mathrm{solv}}(t)$ after a sudden change in the position of the solute charge.

$$\hat{\varepsilon}(\omega) = \varepsilon_\infty' + \frac{\varepsilon - \varepsilon_\infty'}{1 + i\omega\tau}, \qquad (21)$$

where ε is the static dielectric permittivity, ε_∞' is related to the optical dielectric permittivity, and τ is the Debye relaxation time. Equation (21) is a particular case of more general expressions (see, for example, the Havrilak–Negami equation[23]) and it is found to be appropriate for polar solvents, such as water and acetonitrile.

Inserting expression (21) for $\hat{\varepsilon}(\omega)$ in Eq. (18) we obtain for $g_i'(t)$ the integral,

$$g_i'^{D}(t) = \frac{2a_i}{\pi}\frac{A}{\tau}\int_0^\infty d\omega \frac{1}{B^2 + \omega^2}\cos\omega t, \qquad (22)$$

where the constants A and B are

$$A = \frac{-4\pi(\varepsilon - \varepsilon_\infty')}{[4\pi\varepsilon_\infty']^2},$$

$$ \qquad (23)$$

$$B = \frac{1}{\tau}\frac{\varepsilon}{\varepsilon_\infty'}.$$

The solution of the integral in Eq. (22) leads to

$$g_i'^{D}(t) = \frac{Aa_i}{B\tau}e^{-Bt}, \qquad (24)$$

where the exponential decay is due to the use of the Debye model. We note, however, that the decay time of the solvent response (τ') is different (and smaller) from the Debye relaxation time τ, namely, $\tau' \propto \tau\varepsilon_\infty'/\varepsilon$.

When a combined approach is applied, including a fit of the experimental data for the high-frequency portion of the complex dielectric permittivity, the integral in Eq. (18) is solved numerically. We used the treatment of the experimental data fully described in Ref. 24 and there applied to the calculation of the time-dependent Stokes shift. This proce-

dure is more time consuming, but in principle it should provide a more realistic description of the nondiffusive portion of the solvent response.

E. Time-dependent solute-solvent interaction

According to the PCM model, in which solute and solvent mutually polarize, the time evolution of the solvent charges should be coupled to the time evolution of the solute charges and of their potential $\mathbf{V}(t)$ on the cavity.

As anticipated in the introduction and clearly explained by Basilevsky et al.,[9] this coupling would lead to nonlinear effects on the solute polarization. In that case, both the solvent and the solute charges would necessarily become complex valued. To avoid this complication, in the model presented in Sec. II, we have assumed that the time variation of the solute charge and thus of the electric field determining the solvent charge can be approximated with the step function $\theta(t)$. In this way the purely linear response is recovered.

Still keeping this approximation, it is possible to introduce the effects that the time-dependent evolution of the solvent charges has on the solute by including these charges, calculated at time t through Eq. (9), into the Hamiltonian of the solute, as fixed charges.

The resulting wave function and the corresponding density will thus account for the effects of the solvent $\mathbf{q}(t)$ and, as a response, it will give origin to a time-dependent potential $\mathbf{V}(t)$ and to a time-dependent interaction energy $U_{\mathrm{solv}}(t)$,

$$U_{\mathrm{solv}}(t) = \frac{1}{2}[\mathbf{V}(t)]^\dagger\mathbf{q}(t). \qquad (25)$$

F. Application to a simple system

To test the model described in the previous sections, a very simple solute was considered, namely, a point, nonpolarizable charge, moving inside a spherocylindric cavity in a dielectric medium with the same characteristics of liquid water. As for this example, we used the Debye expression (21)
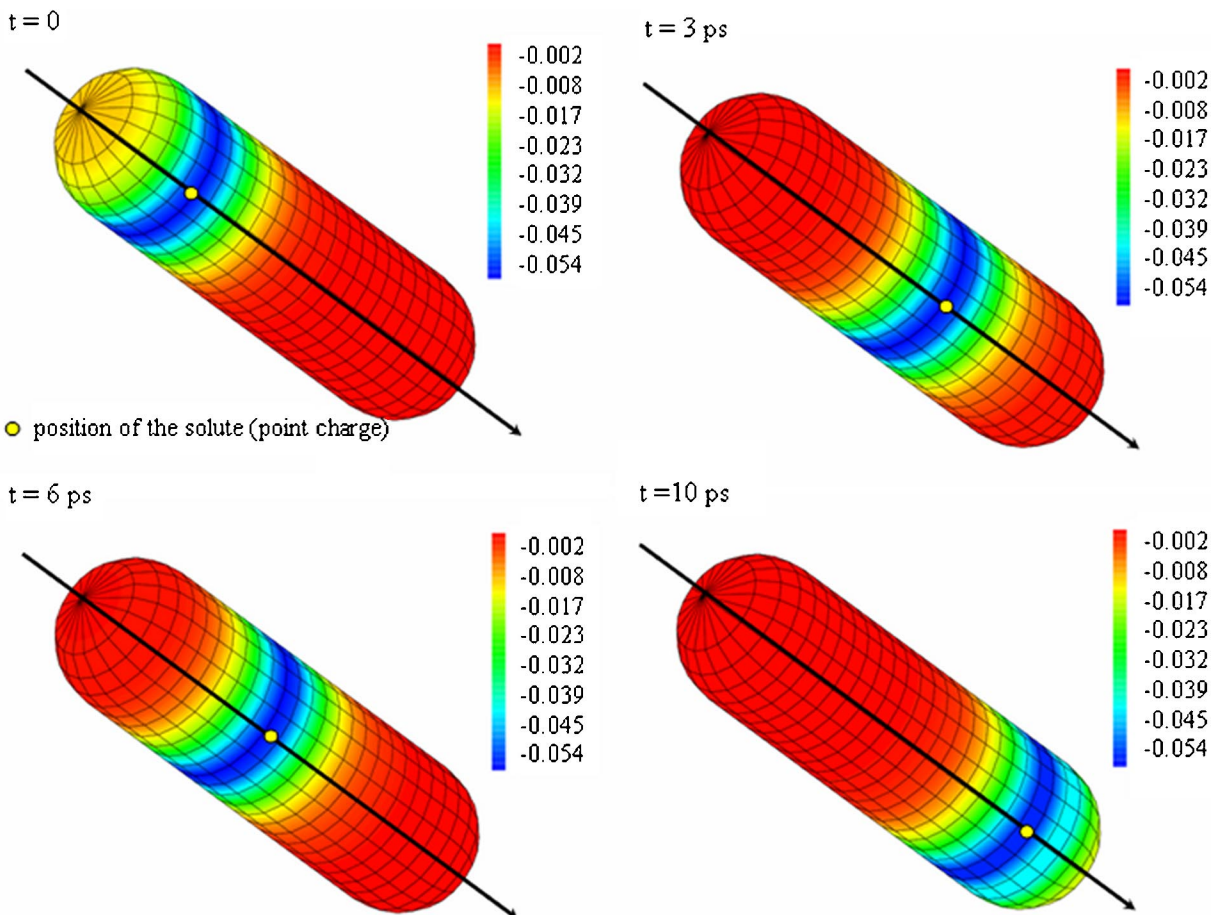
FIG. 3. Time evolution of the apparent charges located on the cavity surface during the slow solute motion. Four main snapshots of the evolution are shown.

to model the frequency dependence of the complex dielectric permittivity ($\varepsilon=78.30, \varepsilon'_\infty=4.21, \tau=8.20$ ps). Two extreme cases were chosen to test the model: (i) a solute which instantaneously reaches the end of the cylinder (fast solute); (ii) a solute which moves so slowly that the solvent is always in equilibrium with it (slow solute).

1. Fast solute

The step variation is described as a change in the position of the point charge on the axis of the cylinder at $t=-\infty$, corresponding to the starting solute-solvent equilibrium, the charge is located at one end of the cylinder, while it is located at the opposite end at $t=0$. After that, we follow the time evolution of the apparent charges on the cavity surface, as we display in Fig. 1.

We chose a representation based on a color scale, qualitatively showing the values of the apparent surface charges. We noticed that, as a consequence of the sudden change in the position of the solute, the solvent rearranges towards a new equilibrium (in this particular case symmetric to the initial one).

In Fig. 2 we also show the evolution of the solute-solvent interaction energy $U_{solv}(t)$ defined in Eq. (25). An instantaneous step change in $U_{solv}(t)$ is shown at $t=0$, followed by an exponential decay, related to the use of the

Debye model of relaxation. Since the system is symmetric, the interaction energy tends to the initial equilibrium value for long times.
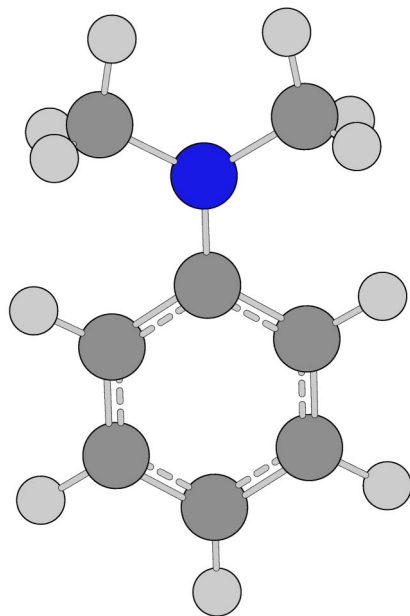
2. Slow solute

Starting from the same equilibrium situation at $t=-\infty$, the charge moves with a constant velocity along the cylinder axis. The velocity was chosen in such a way that the solvent reaches the equilibrium before a new displacement of the solute takes place. We report in Fig. 3 the time evolution of the polarization charges (we omit the snapshot of the initial equilibrium at $t=-\infty$, shown in Fig. 1).

With respect to the previous case, the surface charges follow the position of the solute during its motion. The result obtained for the function $U_{solv}(t)$ is not shown, since the interaction energy is subject to very small variations, which are only related to the position of the solute charge on the axis.

III. IONIZATION OF DMA

In this section we present a study on the variation of the solvation energy profile after an ionization process. As probe system we chose DMA (*N, N*-dimethyl-aniline, shown in Fig. 4) in acetonitrile and in water.

We consider both the direct DMA$\rightarrow$DMA$^+$ and the reverse DMA$^+\rightarrow$DMA processes. In addition to the property

FIG. 4. Structure of N, N-dimethyl-aniline (DMA).

TABLE I. Parameters in Eq. (21) used for water and acetonitrile.

Solvent	ε	ε_∞	ε'_∞	τ (ps)
Water	78.30	1.776	4.210	8.20
Acetonitrile	35.84	1.806	3.510	3.37

$$\lambda_s^d = U_{\text{solv}}^{\text{init,neq}} - U_{\text{solv}}^{\text{init}},$$

$$\lambda_s^r = U_{\text{solv}}^{\text{fin,neq}} - U_{\text{solv}}^{\text{fin}}, \tag{28}$$

where $U_{\text{solv}}^{\text{fin,neq}}$ and $U_{\text{solv}}^{\text{init,neq}}$ are the nonequilibrium interaction energies in the final and in the initial states, respectively.[6,9]

A. Computational details

As we already pointed out, here we neglect the time-dependent evolution of the solute geometry during the solvent relaxation. We have therefore considered the geometry corresponding to the neutral species and the one corresponding to the charged species, both in equilibrium with the solvent. However, as the differences that we have obtained for the time evolution of the solvent response in these two cases are negligible, we therefore present the results obtained for the geometry of the neutral species only. This conclusion is in qualitative agreement with the behavior observed by Sato et al..[15]

We performed geometry optimization at density functional theory (DFT) level using the nonlocal exchange correlation functional by Becke, Lee, Parr, and Yang[29] (B3LYP) with the Dunning/Huzinaga d95v+(d,p) (Ref. 30) basis set in the presence of the solvent (water, acetonitrile) with the PCM model implemented into GAUSSIAN.[31] The cavity surrounding the solute was the result of the superimposition of interlocking spheres centered on atomic sites or groups of atoms. The radii of the spheres were $R(\text{C})=1.925$ Å, $R(\text{CH})=2.125$ Å, $R(\text{CH}_3)=2.525$ Å, and $R(\text{N})=1.840$ Å. We used the same basis set and the same cavity to perform the time-dependent calculation of the polarization charges.

As for the use of the Debye relaxation expression in Eq. (21), we used the value corresponding to the optical dielectric constant $\varepsilon_\infty \approx n^2$ instead of the parameter ε'_∞. This choice was made to have consistence with the time $t=0$ calculation. A different calculation was also run by including the fit of experimental data of $\hat{\varepsilon}(\omega)$: the Debye expression was used in the low-frequency portion of the spectrum, while the fit was

of providing a single-step variation of the solute charge density (exactly as requested by the simple version of the model presented in Sec. II) this particular system was chosen due to the availability of a recent paper[15] studying the same process.

We determine the nonequilibrium free-energy changes as functions of time and in terms of a solvent reaction coordinate, and we calculate the solvent reorganization energy[25] associated with the ionization. By analogy with the definition in Refs. 15, 26, and 27, we define the electrostatic nonequilibrium solvation free energy $\Delta F(t)$ within the harmonic approximation as[28]

$$\Delta F(t) = U_{\text{solv}}(t) - U_{\text{solv}}^{\text{init}} - [\mathbf{V}(t) - \mathbf{V}^{\text{init}}]^\dagger \mathbf{q}(t), \tag{26}$$

where the superscript init refers to values corresponding to the equilibrium situation before the charging process takes place. We also define a solvent reaction coordinate $\Delta S(t)$ as

$$\Delta S(t) = [\mathbf{V}(t) - \mathbf{V}^{\text{init}}]^\dagger \mathbf{q}(t). \tag{27}$$

The definitions for the solvent reorganization energy λ_s which derive from the $t \to \infty$ limit of Eq. (26) for the direct (superscript d) and the reverse (superscript s) processes are
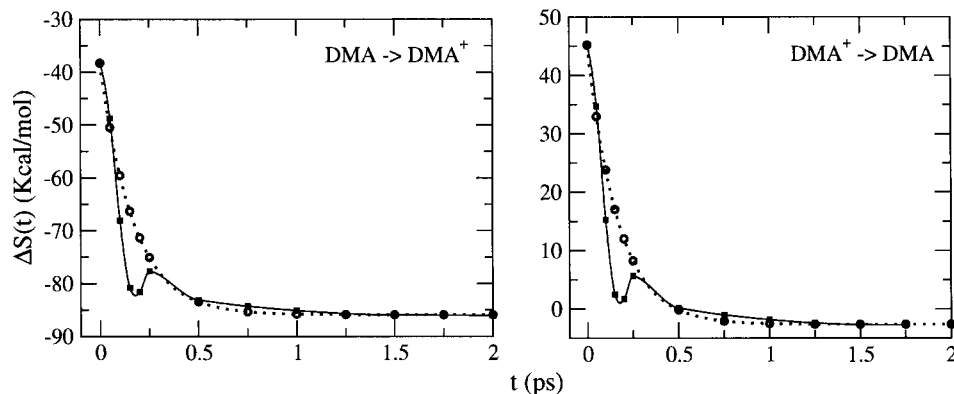

FIG. 5. Evolution of the solvent reaction coordinate as defined in Eq. (27) for (direct, reverse) ionization of DMA in acetonitrile. The open circles, dotted line refer to the procedure based on the Debye expression in Eq. (21) and the full squares, full line refer to the procedure based on fit of the experimental data.
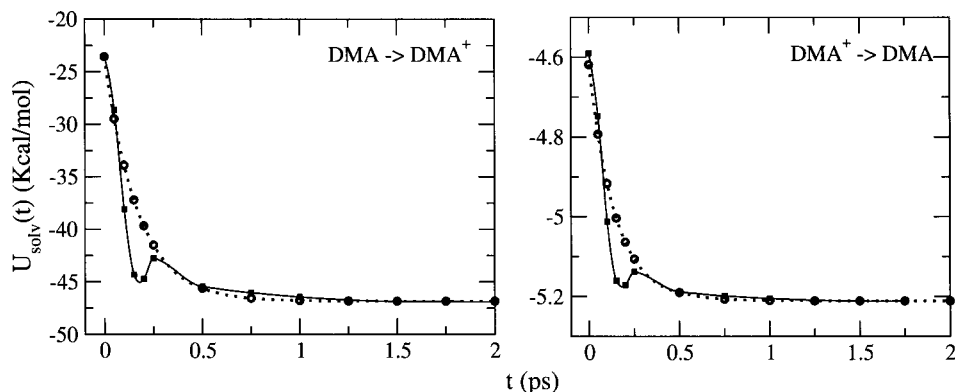
FIG. 6. Time evolution of the interaction energy [see Eq. (25)] for (direct and reverse) ionization of DMA in acetonitrile. The open circles, dotted line refer to the procedure based on the Debye expression in Eq. (21) and the full squares, full line refer to the procedure based on fit of the experimental data.

employed in the high-frequency portion, in which the librational and inertial motions of the solvent are active. In this case, the values of ε'_∞ in Table I were used, according to the procedure used in Ref. 13. We report in Table I the parameters used for water and acetonitrile.

B. Results and discussion

By using Eq. (28), the average values of the reorganization energy $(\lambda_s^d + \lambda_s^r)/2$ obtained here are $\lambda_s = 1.02$ eV in acetonitrile and $\lambda_s = 1.06$ eV in water. The result obtained in Ref. 15 was 1.85 eV (acetonitrile). In the same paper the authors present an estimate for the experimental value of the reorganization energy of the redox pair DMA-duroquinone in a similar solvent (C_3H_7CN), namely, $\lambda_s = 1.39$ eV.

We turn now to discuss the time-dependent properties which characterize the solvent reorganization. We describe in more details the case of acetonitrile as solvent, for which we have a comparison in Ref. 15. It is, however, important to point out that this is a qualitative comparison, being the models employed in the two cases quite different. In fact, the attention of the present study is focused on the solvent relaxation after a step change in the solute charge density, while in Ref. 15 the authors follow a hypothetical linear change in the solute charge density.

1. Acetonitrile

In Fig. 5 we report the time evolution of the solvent reaction coordinate $\Delta S(t)$ [defined in Eq. (27)]. Both the Debye and the experimental $\hat{\varepsilon}(\omega)$ were used.

We notice a different feature in the short time scale in the two cases. The decay related to the Debye expression is

exponential, according to the diffusive relaxation model, while an oscillation is observed in the case of the inclusion of the experimental data. This behavior is the same observed for the solvent response function of acetonitrile calculated with a similar approach,[24] and it has been related to the librational motion of the molecules.

In the direct process (DMA→DMA⁺), ΔS is negative for all times and its absolute value increases with time, reaching a plateau quite rapidly. We anticipate that this behavior is common to all time-dependent properties that we calculated. On the other hand, in the reverse process (DMA⁺→DMA), ΔS starts with highly positive values and is positive before reaching the plateau, when it becomes slightly negative. The interpretation of this behavior is based on Eq. (27): (i) in the direct case, ΔS has negative values because the dominant term is the negative $[\mathbf{V}(t)]^\dagger \mathbf{q}(t)$, being $\mathbf{V}^{init}$ as the potential corresponding to the neutral molecule, which is conceivably negligible with respect to $\mathbf{V}(t)$. (ii) By contrast, in the reverse case, the dominant term is $(\mathbf{V}^{init})^\dagger \mathbf{q}(t)$, being $\mathbf{V}^{init}$ as the potential of the charged molecule; in this case ΔS decreases with increasing t, since the values of $\mathbf{q}(t)$ approach the ones induced by the neutral molecule (which are very small).

In Fig. 6 we report a plot, the time dependence of U_{solv} defined in Eq. (25), which confirms the considerations we have just exposed.

Although the shape of the relaxation is the same in the direct and in the reverse case, in the latter the global variation of U_{solv} is much smaller than in the former. In fact, in the reverse case, at $t=0$, U_{solv} is determined by the potential $\mathbf{V}(0)$ of the neutral DMA and the values of $\mathbf{q}(t)$ decrease toward the corresponding equilibrium charges. On the con-
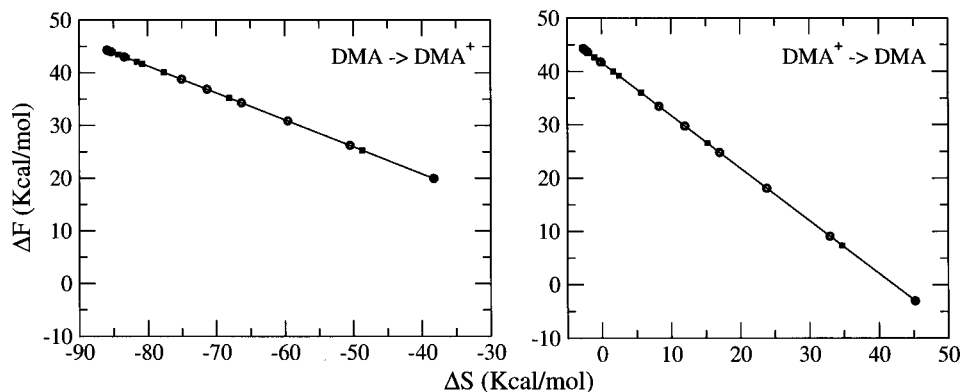

FIG. 7. Nonequilibrium free-energy profile [see Eq. (26)] as a function of the solvent reaction coordinate, defined in Eq. (27), after (direct, reverse) ionization of DMA in acetonitrile. The open circles, dotted line refer to the procedure based on the Debye expression in Eq. (21) and the full squares, full line refer to the procedure based on fit of the experimental data.
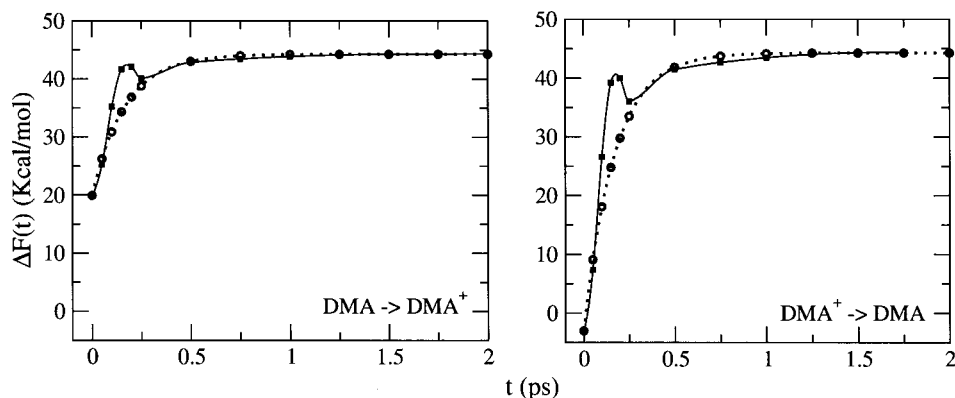
FIG. 8. Time evolution of the non-equilibrium free-energy profile as defined in Eq. (26) after (direct, reverse) ionization of DMA in acetonitrile. The open circles, dotted line refer to the procedure based on the Debye expression in Eq. (21) and the full squares, full line refer to the procedure based on fit of the experimental data.

trary, in the direct process, $U_{solv}(0)$ is determined by the potential $\mathbf{V}(0)$ of the charged species and this time the values of $\mathbf{q}(t)$ increase toward those corresponding to DMA$^+$.

The comparison of the functions plotted in Figs. 5 and 6 with the corresponding ones (Fig. 3) in Ref. 15 is not straightforward, as we already mentioned. The variation of the solvent reaction coordinate follows a linear dependence on the parameter which characterizes the evolution from the neutral to the charged molecule (and vice versa). In the present case, we observe a decay, being the reaction coordinate, the expression of the solvent rearrangement after the charged (neutral) state has been reached. This decay reflects the exponential decay of the solvent polarization, as described by the Debye expression in Eq. (21).

The dependence of ΔF on the solvent reaction coordinate ΔS is shown in Fig. 7, while in Fig. 8 the time dependence of this function is displayed.

As it can be seen from Fig. 7, a linear dependence of ΔF on ΔS is obtained: we note that this linearity comes from the combination of the two terms (ΔU_{solv} and ΔS) which show the same time-dependent behavior. In fact, as displayed in Fig. 8, the nonequilibrium free-energy profile as a function of t features a similar shape to those obtained for U_{solv} and ΔS.

In Fig. 7, the slope of the two lines is different and the two graphs are not symmetric. This is due to the fact that, even though the extent of the change [$\Delta \mathbf{E}$ in Eq. (7)] is the same in the two processes, the situation in which it takes place is different. In the first case, the solvent is in equilibrium with the neutral solute, while in the second case it is in equilibrium with the charged solute. As already commented,

ΔS is negative and its absolute value increases with increasing t in the direct process, while it becomes smaller in the reverse process.

2. Water

In Figs. 9 and 10 we report the time-dependent behavior of U_{solv} and of $\Delta F(\Delta S)$ obtained in water.

Being similar to the corresponding ones in acetonitrile, we omit a detailed description of the behavior of the functions considered and only $U_{solv}(t)$ and the dependence of ΔF on the solvent reaction coordinate ΔS are discussed. Differences of the order of only a few Kcal/mol are found between the two solvents as for the initial and the final (equilibrium) states. These small differences are due to the fact that both solvents are highly polar (as shown by the high static value of the dielectric constant) and thus in an electrostatic model as that considered here their effects are quite similar.

We note, however, that the time evolution in water is slightly slower than in acetonitrile either in the result based on the Debye expression and in one based on the experimental data. Solvation dynamics in acetonitrile is faster than in water, as it can be noticed from the smaller relaxation time τ in the Debye expression (21). In water, the relaxation related to the fit of the experimental data is faster in the shorter time scale. It has been already pointed out[13,24] on the basis of the comparison of the calculated solvation relaxation function with the experimental Stokes shift that the procedure based on the experimental data allows a better description of the inertial portion of the decay.

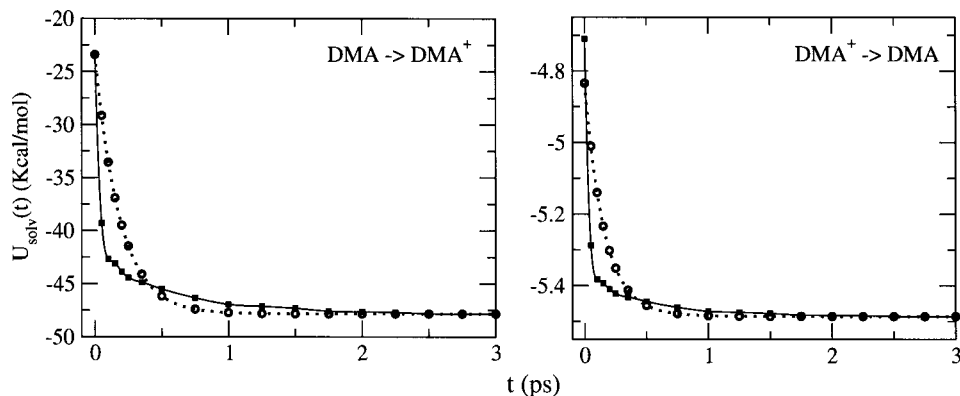In addition, by including a more realistic description of

FIG. 9. Time evolution of the interaction energy [see Eq. (25)] for (direct and reverse) ionization of DMA in water. The open circles, dotted line refer to the procedure based on the Debye expression in Eq. (21) and the full squares, full line refer to the procedure based on fit of the experimental data.
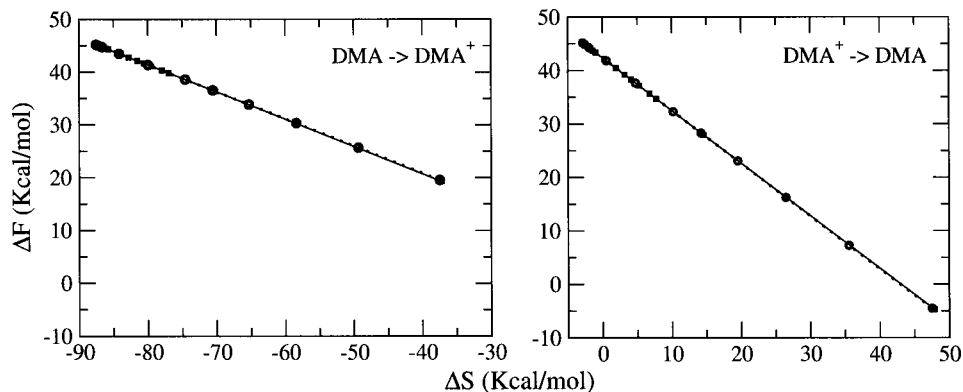
FIG. 10. Nonequilibrium free-energy profile [see Eq. (26)] as a function of the solvent reaction coordinate, defined in Eq. (27), after (direct, reverse) ionization of DMA in water. The open circles, dotted line refer to the procedure based on the Debye expression in Eq. (21) and the full squares, full line refer to the procedure based on fit of the experimental data.

the dielectric properties of the solvents, it is possible to observe more differences in the time-dependent properties of the solvation response. The same cannot be said in the case of the Debye-based results, which tend to be very similar in shape.

IV. SUMMARY AND CONCLUSIONS

In this paper we presented a methodology designed to follow the time evolution of the solvent polarization after a change in the solute charge density. We worked within a continuum representation of the solvent in which we included its dynamics through the complex dielectric permittivity $\hat{\varepsilon}(\omega)$ as a function of the frequency.

We applied the model to a quantum-mechanical solute and to a process in which the time scale of the solute change is much smaller than the one of the solvent response. However, we note that the model can be generalized to more complex situations, for which we have presented the necessary theoretical background (see Sec. II).

The process that we analyzed is the ionization of DMA, and its reverse decharging process, in acetonitrile and in water. Starting from the initial equilibrium state, we followed the solvent relaxation through the definition of a solvent reaction coordinate until the new equilibrium state was reached. The behavior of the two solvents was quite similar, since their polarization response rapidly decay, as expected. We observed some differences in the shape of the decay through the results obtained with variants of the method. The first one was based on the Debye theory of relaxation, which emphasizes the diffusive portion of the relaxation, while the second one took advantage of the experimental data of absorption in order to achieve a better description of the short-time, inertial portion. In this second case, the acetonitrile response was characterized by an oscillation, which is due to the librational motions: the second procedure therefore allows a more specific description of each particular solvent. In fact, the correspondent feature related to libration in water has the shape of a broad shoulder. On the other hand, this methodology is more expensive from a computational point of view, since it requires to process the ω-dependent expressions through a numerical (anti-)Fourier transform, while the Debye theory provides an analytical expression for $\hat{\varepsilon}(\omega)$.

This work represents a first step towards the description of a real time-dependent evolution of the solvent, in which

the solute relaxation is included as well. Some important developments are still to be completed following two main directions.

On the one hand, we can define a strategy to properly treat the time-dependent evolution of the solute-solvent mutual polarization. This strategy could in fact resort to a discretization of the solute time-dependent change in terms of multiple steps (see Sec. II C). A similar extension of the model would, for example, permit to study the coupling of the solvent relaxation with that of a solute excited state.

On the other hand, the multistep version of the model can be interfaced with real time-dependent methodologies as, for example, molecular-dynamics simulations.

[1] J. D. Simon, Acc. Chem. Res. **21**, 128 (1988).
[2] M. Maroncelli, J. Mol. Liq. **57**, 1 (1993).
[3] R. M. Stratt and M. Maroncelli, J. Phys. Chem. **100**, 12981 (1996).
[4] B. Bagchi, Annu. Rev. Phys. Chem. **40**, 115 (1989).
[5] B. M. Ladanyi *Theoretical methods in condensed phase chemistry* (Kluwer, Dordrecht, the Netherlands, 2000), Chap. 7.
[6] B. Mennucci, R. Cammi, and J. Tomasi, J. Chem. Phys. **109**, 2798 (1998).
[7] R. Cammi and B. Mennucci, J. Chem. Phys. **110**, 9877 (1999).
[8] R. Cammi, B. Mennucci, and J. Tomasi, J. Phys. Chem. A **104**, 6531 (2000).
[9] M. V. Basilevsky, D. F. Parsons, and M. V. Vener, J. Chem. Phys. **108**, 1103 (1998).
[10] I. V. Rostov, M. V. Basilevsky, and M. D. Newton, *Simulation and Theory of Electrostatic Interactions in Solution*, edited by L. R. Pratt and G. Hummer (American Institute of Physics, New York, 1999).
[11] P. G. Wolynes, J. Chem. Phys. **86**, 5133 (1987).
[12] M. D. Newton and H. L. Friedman, J. Chem. Phys. **88**, 4460 (1988).
[13] C. P. Hsu, X. Song, and R. A. Marcus, J. Phys. Chem. B **101**, 2546 (1997).
[14] S. Chong, S. Miura, G. Basu, and F. Hirata, J. Phys. Chem. **99**, 10526 (1995).
[15] H. Sato, Y. Kobori, S. Tero-Kubota, and F. Hirata, J. Chem. Phys. **119**, 2753 (2003).
[16] H. Sato, Y. Kobori, S. Tero-Kubota, and F. Hirata, J. Phys. Chem. B **108**, 11709 (2004).
[17] J. Tomasi and M. Persico, Chem. Rev. **94**, 2027 (1994).
[18] V. Barone and M. Cossi, J. Phys. Chem. A **102**, 1995 (1998).
[19] B. Mennucci, E. Cancès, and J. Tomasi, J. Chem. Phys. **101**, 10506 (1997).
[20] G. Scalmani, V. Barone, K. N. Kudin, C. S. Pomelli, G. E. Scuseria, and M. J. Frisch, Theor. Chem. Acc. **111**, 90 (2004).
[21] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, London, 1976).
[22] R. Kubo, J. Phys. Soc. Jpn. **12**, 570 (1957).
[23] C. J. F. Böttcher, *Theory of Electric Polarization* (Elsevier, Amsterdam, 1952).
[24] F. Ingrosso, B. Mennucci, and J. Tomasi, J. Mol. Liq. **108**, 21 (2003).
[25] R. A. Marcus, Rev. Mod. Phys. **65**, 599 (1993).
[26] M. V. Vener, I. V. Leontyev, Y. A. Dyakov, M. V. Basilevsky, and M. D.

Newton, J. Phys. Chem. B **106**, 13078 (2002).

[27]S. Chong and F. Hirata, J. Chem. Phys. **106**, 5225 (1997).

[28]We note that in Eq. (26) we have omitted a time independent term, namely $U_{\text{solv}}^{\text{init,dyn}} + U_{\text{solv}}^{\text{fin,dyn}} - (\mathbf{V}^{\text{init}})^{\dagger}\mathbf{q}^{\text{fin,dyn}}$, where the label *dyn* indicates that the corresponding quantities ($\mathbf{V}$ or $\mathbf{q}$) are obtained using ε_{∞} instead of ε.

[29]A. Becke, J. Chem. Phys. **98**, 5648 (1993).

[30]T. H. Dunning, Jr. and P. J. Hay, *Modern Theoretical Chemistry*, edited by H. F. Shaefer III (Plenum, New York, 1976), Vol. 3.

[31]M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 2003, Revision B.03, Gaussian, Inc., Pittsburgh, PA, 2003.