

## ARTICLE

# Continuum Model for Electronic Polarization Based on a Novel Dielectric Response Function

Quan-de Wang, Han-yu Wu, Ke-xiang Fu, Xiang-yuan Li\*

College of Chemical Engineering, Sichuan University, Chengdu 610065, China

(Dated: Received on June 11, 2009; Accepted on August 10, 2009)

A generalized response function based on the use of dielectric spectra for dielectric relaxation process is derived. We apply the general response function to the special case in order to examine how special dielectric relaxation functions developed by other authors for solvent relaxation can be derived based on our formulations. Three typical solvents, water, methanol, and acetonitrile are used to investigate the electronic polarization processes of polar solvents. The solvent electronic polarization process is shown after a linear variation with the external electric field imposed on the solvent. The results show a conclusion that the electronic polarization of the solvents will accompany the electronic transition synchronously, without time lag.

**Key words:** Response function, Dielectric relaxation, Electronic polarization, Continuum model

## I. INTRODUCTION

In the past half century, an explosive growth in the study of chemical dynamics has been made, spurred by advances in both experimental and theoretical techniques. Now the research of chemical dynamics is focused on how it is affected by the interaction with the environment. Understanding solvation dynamics, *i.e.*, the response of the solvent to changes in solute size and/or solute charge distribution is an essential step to fully understand chemical dynamics in condensed phases. It is therefore not surprising that a great deal of research has been devoted to solvation dynamics and considerable progress has been made in elucidating the mechanisms of solvation dynamics and its effect on chemical reactions through experiments, theory, and computer simulations [1–20].

In order to investigate solvation dynamics and many other chemical and biochemical reactions in condensed phases, polarization is an important concept. The dielectric relaxation of solvent is a measurement of the collective polarization of all the polar solvent molecules. Generally, the polarization of a system to reach the final (equilibrium) state after an external field is switched on/off is usually divided into two parts: electronic and orientational [7]. The electronic polarization is usually assumed to be instantaneous. There have been several approaches to modeling dielectric relaxation [5–20]. In recent years, considerable progress has been made

in predicting the time evolution of the solvation response by using the relaxation properties of the solvent as input and these methods have also been coupled to quantum mechanical (QM) continuum solvation models [12,13,17–20]. The noticeably work was originally developed by Hsu *et al.* within such a scheme the continuum solvation model is used to calculate the solute-solvent interaction and experimental data of the solvent dielectric spectra are introduced as dynamical input to describe dielectric relaxation [12]. This model was soon reformulated and coupled to QM continuum solvation model, the polarizable continuum model (PCM) [13,17,19]. Subsequently, the same model has been extended to describe a general time-dependent relaxation of the solvent within the PCM [18–20]. The results obtained correlate well with experimental results and confirm the validity of continuum model to the treatment of solvation dynamics. Despite their successes in the description of the dynamics of orientational polarization by means of continuum solvation model, few works have been done for electronic polarization.

In this work, we present a generalized dielectric response function to describe the polarization relaxation of dielectric media. Based on continuum solvation model, we have applied the generalized response function to special cavity model which plays a central role in practice. The derived time-correlation polarization relaxation function is the same as the previous results. As an application of the novel response function, adopting the experimentally measured frequency-dependent dielectric permittivity,  $\epsilon(\omega)$ , we have investigated the dielectric response functions and the electronic polarization process for polar solvents. In the present work, water, methanol, and acetonitrile are taken as the ex-

---

\* Author to whom correspondence should be addressed. E-mail: xyli@scu.edu.cn

amples to verify the developed model.

## II. THE GENERAL DIELECTRIC RESPONSE FUNCTION FOR DIELECTRIC RELAXATION

In very rapidly varying fields, the relationship between dielectric displacement  $\mathbf{D}$  and electric field  $\mathbf{E}$  are considered to be linear, based on the theory of electrodynamics of continuous media [21]. The general linear relation between  $\mathbf{D}(t)$  and the values of function  $\mathbf{E}(t)$  at all previous instants can be written in the integral form [21]

$$\mathbf{D}(t) = \mathbf{E}(t) + \int_0^\infty f(\tau)\mathbf{E}(t-\tau)d\tau \quad (1)$$

where  $f(\tau)$  is a function of time and depends on the properties of the medium [21]. Taking the Fourier and inverse Fourier transforms of Eq.(1), we have the following relations,

$$\mathbf{D}(\omega) = \varepsilon(\omega)\mathbf{E}(\omega) \quad (2)$$

$$\varepsilon(\omega) = 1 + \int_0^\infty f(\tau) \exp(i\omega\tau)d\tau \quad (3)$$

$$f(\tau) = \frac{1}{2\pi} \int_{-\infty}^\infty [\varepsilon(\omega) - 1] \exp(-i\omega\tau)d\omega \quad (4)$$

Based on the theory of electrodynamics of continuous media [21], the linear relation between the polarization,  $\mathbf{P}$ , and a uniform external field,  $\mathbf{E}$ , is  $\mathbf{P}=\chi\mathbf{E}$ . This is an important relation, even though it doesn't involve the time-dependent properties of continuous media. Here, in order to investigate the dielectric relaxation process of media, the formulism has been generalized to be time-dependent and a novel dielectric response function has been established.

If the retardation effect of the electric field with the location of the space can be ignored, the charge changes of the dielectric medium would change instantaneously with the electric field variation. In order for simplicity, we consider a step function change in the uniform electric field imposed on the medium:

$$\mathbf{E}_0(t) = \begin{cases} \mathbf{E}_{10}, & (t < 0) \\ \mathbf{E}_{20}, & (t \geq 0) \end{cases} \quad (5)$$

in which the subscript "0" refers to the vacuum electric field, which can be resulted from the existence of the solute charge.

As the polarization of the dielectric medium cannot change instantaneously as a result of the inertial effect, the corresponding polarization charges cannot have a mutation, and hence the polarization electric field resulted from the polarization charges cannot be synchronized with the vacuum electric field. If the retardation effect of polarization charges and its resulting electric field can be ignored, the polarization can also be synchronized with the polarization electric field. We have

shown (see Appendix A) that in the study of solvation dynamics based on continuum solvation model, it is reasonable to ignore the retardation effect and to deal with the electromagnetic field of the solute-solvent system as an electrostatic field. Thus, based on linear response theory, the general relation between the polarization,  $\mathbf{P}(t)$ , and the values of function  $\mathbf{E}(t)$  at all previous instants can be written in the following integral form, *i.e.*, [20–23,26]

$$\mathbf{P}(t) = \int_0^\infty \vec{\mathbf{f}}(\tau) \cdot \mathbf{E}_0(t-\tau)d\tau \quad (6)$$

Taking the Fourier transform of Eq.(6), we obtain the following relation,

$$\mathbf{P}(\omega) = \vec{\mathbf{R}}(\omega) \cdot \mathbf{E}_0(\omega) \quad (7)$$

where  $\vec{\mathbf{R}}(\omega)$  is defined as

$$\vec{\mathbf{R}}(\omega) = \int_{-\infty}^{+\infty} \vec{\mathbf{f}}(\tau) \exp(i\omega\tau)d\tau \quad (8)$$

The inverse Fourier transform of Eq.(8) is given as the following expression for  $\vec{\mathbf{f}}$ ,

$$\vec{\mathbf{f}}(\tau) = \frac{1}{2\pi} \int_{-\infty}^\infty \vec{\mathbf{R}}(\omega) \exp(-i\omega\tau)d\omega \quad (9)$$

In Eqs. (6)–(9),  $\vec{\mathbf{f}}$  and  $\vec{\mathbf{R}}$  are generally taken as tensors. Eqs. (6), (7), and (9) are the basic and general formulations in the investigation of dielectric relaxation process of dielectric medium based on linear response approximation. Substituting Eq.(5) into Eq.(6) and noticing the integral interval, we have

$$\mathbf{P}(t) = \int_t^\infty \vec{\mathbf{f}}(\tau)d\tau \cdot \mathbf{E}_{10} + \int_0^t \vec{\mathbf{f}}(\tau)d\tau \cdot \mathbf{E}_{20} \quad (10)$$

Based on the theory of equilibrium electrostatic field and noting that the general frequency-dependent relationship can be determined through Eq.(7), we can obtain the following expressions, *i.e.*,

$$\begin{aligned} \mathbf{P}_1^{\text{eq}} &= \vec{\mathbf{R}}_1(0) \cdot \mathbf{E}_{10} \\ \mathbf{P}_2^{\text{eq}} &= \vec{\mathbf{R}}_2(0) \cdot \mathbf{E}_{20} \end{aligned} \quad (11)$$

where  $\mathbf{P}_1^{\text{eq}}$  and  $\mathbf{P}_2^{\text{eq}}$  denote the equilibrium polarizations corresponding to  $\mathbf{E}_{10}$  and  $\mathbf{E}_{20}$ , respectively. Similarly, based on our above assumption of ignoring the retardation effect of the electric field with respect to the charge location in space, we have

$$\begin{aligned} \mathbf{P}_1(\omega) &= \vec{\mathbf{R}}_1(\omega) \cdot \mathbf{E}_{10}(\omega) \\ \mathbf{P}_2(\omega) &= \vec{\mathbf{R}}_2(\omega) \cdot \mathbf{E}_{20}(\omega) \end{aligned} \quad (12)$$

Combining Eqs. (10) and (11) leads to

$$\mathbf{P}(t) = \vec{\mathbf{F}}_1(t) \cdot \mathbf{P}_1^{\text{eq}} + [\vec{\mathbf{I}} - \vec{\mathbf{F}}_2(t)] \cdot \mathbf{P}_2^{\text{eq}} \quad (13)$$

Here  $\vec{\mathbf{I}}$  is the unit tensor, and we still have the following relations,

$$\begin{aligned} F_{1j}(t) &= B_{1j} \int_t^\infty f_{1j}(\tau) d\tau, \quad (j = 1, 2, 3) \\ F_{2j}(t) &= B_{2j} \int_t^\infty f_{2j}(\tau) d\tau, \quad (j = 1, 2, 3) \end{aligned} \quad (14)$$

Eq.(14) is defined as the integral formulation of  $\vec{\mathbf{f}}(\tau)$ , and  $B$  is the normalized factor that makes Eq.(15) hold,

$$\begin{aligned} B_{1j} \int_0^\infty f_{1j}(\tau) d\tau &= 1 \\ B_{2j} \int_0^\infty f_{2j}(\tau) d\tau &= 1 \\ \vec{\mathbf{F}}_1(\infty) &= 0, \quad \vec{\mathbf{F}}_2(\infty) = 0 \end{aligned} \quad (15)$$

In which the following equations hold by means of Eq.(9),

$$\vec{\mathbf{f}}_1(\tau) = \frac{1}{2\pi} \int_{-\infty}^\infty \vec{\mathbf{R}}_1(\omega) \exp(-i\omega\tau) d\omega \quad (16)$$

$$\vec{\mathbf{f}}_2(\tau) = \frac{1}{2\pi} \int_{-\infty}^\infty \vec{\mathbf{R}}_2(\omega) \exp(-i\omega\tau) d\omega \quad (17)$$

As the polarization field  $\mathbf{E}^P(t)$  is synchronous with the polarization, it can be written similarly to Eq.(13) as follows

$$\mathbf{E}^P(t) = \vec{\mathbf{F}}_1(t) \cdot \mathbf{E}_{1p}^{\text{eq}} + [\vec{\mathbf{I}} - \vec{\mathbf{F}}_2(t)] \cdot \mathbf{E}_{2p}^{\text{eq}} \quad (18)$$

in which  $\mathbf{E}_{jp}^{\text{eq}}(\mathbf{r})$  ( $j=1,2$ ) can be expressed as

$$\mathbf{E}_{jp}^{\text{eq}}(\mathbf{r}) = \int_{V'} \frac{\rho_{jp}^{\text{eq}}(\mathbf{r}')(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} dV' + \oint_{S'} \frac{\sigma_{jp}^{\text{eq}}(\mathbf{r}')(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} dS' \quad (19)$$

( $j = 1, 2$ )

In Eq.(19),  $\rho_{jp}^{\text{eq}}$  and  $\sigma_{jp}^{\text{eq}}$  stand for the volume distribution of polarized charge and the surface one for equilibrium state  $j$  ( $j=1,2$ ), respectively. The time-dependent field  $\mathbf{E}(t)$  and electric displacement  $\mathbf{D}(t)$  take the following forms,

$$\mathbf{E}(t) = \mathbf{E}_0(t) + \mathbf{E}^P(t) \quad (20)$$

$$\mathbf{D}(t) = \mathbf{E}(t) + 4\pi\mathbf{P}(t) \quad (21)$$

### III. DIELECTRIC RELAXATION BY CONTINUUM SOLVATION MODEL

We apply the generalized dielectric response function to some simple cases that were investigated in the research of solvation dynamics by other authors. We can see that previous implementations [18–20] of polarization relaxation functions in the research of solvation dynamics or time-dependent solvation can be reproduced by the present generalized formulations.

First, we consider the common case based on the continuum solvation model [24]. In the most widely used continuum solvation model, the polarizable continuum model (PCM), the solvent is represented by a continuum dielectric medium within which a cavity is built to bath the solute. In practical implementation of PCM, the cavity surface is partitioned into small domains, called “tesserae”, and the continuous surface charge is cut into discrete set of point charges lying on the tesserae. At the boundary of two regions I and II, there is an apparent surface charge (ASC) distribution given by

$$\sigma(\mathbf{r}, t) = \mathbf{n} \cdot [\mathbf{P}_I(\mathbf{r}, t) - \mathbf{P}_{II}(\mathbf{r}, t)] \quad (22)$$

in which  $\mathbf{n}$  is the unit vector at the boundary surface pointing from region I to region II. If we assume that all the surface distribution of polarization charge  $\sigma$  is limited to the cavity surface, Eq.(6) can be rewritten as

$$\sigma(\mathbf{r}, t) = \int_0^\infty f(\mathbf{r}, \tau) \mathbf{n} \cdot \mathbf{E}_0(\mathbf{r}, t - \tau) d\tau \quad (23)$$

Similarly, taking the Fourier and inverse Fourier transforms of Eq.(23), we can obtain the following expressions, *i.e.*,

$$\begin{aligned} \sigma(\mathbf{r}, \omega) &= \chi_1(\omega) \mathbf{n} \cdot \mathbf{E}_I(\mathbf{r}, \omega) - \chi_2(\omega) \mathbf{n} \cdot \mathbf{E}_{II}(\mathbf{r}, \omega) \\ &= R(\mathbf{r}, \omega) \mathbf{n} \cdot \mathbf{E}_0(\mathbf{r}, \omega) \end{aligned} \quad (24)$$

$$R(\mathbf{r}, \omega) = \int_{-\infty}^{+\infty} f(\mathbf{r}, t) \exp(i\omega\tau) d\tau \quad (25)$$

$$f(\mathbf{r}, \tau) = \frac{1}{2\pi} \int_{-\infty}^\infty R(\mathbf{r}, \omega) \exp(-i\omega\tau) d\omega \quad (26)$$

Substituting Eq.(5) into Eq.(23) leads to

$$\sigma(\mathbf{r}, t) = \int_t^\infty f_1(\mathbf{r}, \tau) d\tau \mathbf{n} \cdot \mathbf{E}_{10} + \int_0^t f_2(\mathbf{r}, \tau) d\tau \mathbf{n} \cdot \mathbf{E}_{20} \quad (27)$$

For equilibrium state, the following relation holds, *i.e.*,

$$\begin{aligned} \sigma_{10}(\mathbf{r}, 0) &= R_1(\mathbf{r}, 0) \mathbf{n} \cdot \mathbf{E}_{10}(\mathbf{r}) \\ \sigma_{20}(\mathbf{r}, 0) &= R_2(\mathbf{r}, 0) \mathbf{n} \cdot \mathbf{E}_{20}(\mathbf{r}) \end{aligned} \quad (28)$$

Combining Eqs. (27) and (28), we can get

$$\sigma(\mathbf{r}, t) = F_1(\mathbf{r}, t) \sigma_1^{\text{eq}}(\mathbf{r}) + [1 - F_2(\mathbf{r}, t)] \sigma_2^{\text{eq}}(\mathbf{r}) \quad (29)$$

where  $F_j(\mathbf{r}, t)$  is defined as

$$F_j(\mathbf{r}, t) = B_j \int_t^\infty f_j(\mathbf{r}, \tau) d\tau, \quad (j = 1, 2) \quad (30)$$

and  $\sigma_1^{\text{eq}}(\mathbf{r})$  and  $\sigma_2^{\text{eq}}(\mathbf{r})$  stand for the surface distribution of the polarization charge of equilibrium states 1 and 2, respectively. Inserting Eq.(26) into Eq.(30), we have

$$F_j(\mathbf{r}, t) = \frac{B_j}{2\pi} \int_t^\infty \int_{-\infty}^\infty R_j(\mathbf{r}, \omega) \exp(-i\omega\tau) d\omega d\tau \quad (31)$$

Analytically solving Eq.(31) (see Appendix B) yields the following result,

$$F_j(\mathbf{r}, t) = \frac{B_j}{\pi} \int_0^\infty \frac{[R_j(\mathbf{r}, \omega) - R_j(\mathbf{r}, 0)] \exp(-i\omega t)}{i\omega} d\omega$$

$$= \frac{2B_j}{\pi} \int_0^\infty \frac{\cos(\omega t)}{\omega} \text{Im}[R_j(\mathbf{r}, \omega)] d\omega \quad (32)$$

where Im indicates the imaginary part of  $R_j(\mathbf{r}, \omega)$ . Generally, the frequency-dependent response function  $R_j(\mathbf{r}, \omega)$  is related to the structure of the cavity, the charge distribution in the cavity and the dielectric permittivity  $\varepsilon(\omega)$  of the medium.

In continuum solvation model, the solvent is basically taken to be isotropic and homogeneous. Therefore, the response is the same in all directions, that is,  $\mathbf{E}_0$ ,  $\mathbf{P}$ , and  $\mathbf{E}$  are parallel. Eq.(6) can be reduced to

$$\sigma(t) = \mathbf{n} \cdot \mathbf{P}(t)$$

$$= \int_0^\infty f(\tau) \mathbf{n} \cdot \mathbf{E}_0(t - \tau) d\tau \quad (33)$$

This is just the arbitrary cavity problem in continuum solvation model that has been previously used to the study of time-dependent solvation. Similarly to the above expression, we can finally get

$$F(t) = \frac{2B}{\pi} \int_0^\infty \frac{\cos(\omega t)}{\omega} \text{Im}[R(\omega)] d\omega \quad (34)$$

here  $\vec{\mathbf{f}}$  and  $\mathbf{F}(\mathbf{r}, t)$  have been simplified to scalar functions under the condition of isotropic and homogeneous solvent. The results are similar to the previous expressions except for a normalized factor  $B$  [18–20].

As  $\mathbf{P}$  is synchronized with the polarization electric field, based on Eqs. (13) and (18), the polarization and the polarized electric field are expressed as

$$\mathbf{P}(t) = F(t) \mathbf{P}_1^{\text{eq}} + [1 - F(t)] \mathbf{P}_2^{\text{eq}} \quad (35)$$

$$\mathbf{E}^{\text{p}}(t) = \mathbf{E}_{1\text{p}}^{\text{eq}} F(t) + \mathbf{E}_{2\text{p}}^{\text{eq}} [1 - F(t)] \quad (36)$$

By using Eqs. (20) and (21),  $\mathbf{E}(t)$  and  $\mathbf{D}(t)$  take the following expressions,

$$\mathbf{E}(t) = \begin{cases} \mathbf{E}_{10} + \mathbf{E}_{1\text{p}}^{\text{eq}}, & (t < 0) \\ \mathbf{E}_{20} + \mathbf{E}_{1\text{p}}^{\text{eq}} F(t) + \mathbf{E}_{2\text{p}}^{\text{eq}} [1 - F(t)], & (t \geq 0) \end{cases} \quad (37)$$

$$\mathbf{D}(t) = \begin{cases} \mathbf{E}_{10} + \mathbf{D}_{1\text{p}}^{\text{eq}}, & (t < 0) \\ \mathbf{E}_{20} + \mathbf{D}_{1\text{p}}^{\text{eq}} F(t) + \mathbf{D}_{2\text{p}}^{\text{eq}} [1 - F(t)], & (t \geq 0) \end{cases} \quad (38)$$

$$\mathbf{D}_\text{p}^{\text{eq}} = \mathbf{E}_\text{p}^{\text{eq}} + 4\pi \mathbf{P}^{\text{eq}} \quad (39)$$

Starting at the equilibrium state 1, the system undergoes a sudden change of its charge distribution at  $t=0$ , then the system is driven to the non-equilibrium state 2. When the time goes to infinity, the non-equilibrium state 2 finally relaxes to a new equilibrium state 2. Thus, Eqs. (35)–(38) represent the polarization, polarized electric field, total electric field and dielectric displacement at any time in non-equilibrium state 2, respectively.

#### IV. ELECTRONIC POLARIZATION OF POLAR SOLVENT

Up to now, most studies on dielectric relaxation process concentrate on the molecular orientational polarization, not involving the relaxation process of electronic polarization process versus the time. The electronic polarization response of solvent to an applied electric field is an interesting topic while it has not been amply addressed, except some mean-field arguments in the work such as by Marcus [27], Marchi *et al.* [28], and later by Kim *et al.* and Hynes *et al.* [29–31]. We apply the dielectric response function to electronic polarization based on continuum model by using the frequency-dependent complex dielectric permittivity in terms of collectively experimental complex refractive index. However, in the present approach, it should be kept in mind that the coupling between the electronic transition of the probe molecule and the solvent electronic polarization is not taken into account. Therefore, the issue studied in this work should be considered as the pure solvent electronic polarization. In order to investigate this ultrafast process, we assume that the charge distribution of the solute changes linearly with time which means that the electric field takes the following expression,

$$\mathbf{E}_0(t) = \begin{cases} \mathbf{E}_{10}, & (t < 0) \\ \mathbf{E}_{10} + \frac{t}{\tau_s} (\mathbf{E}_{20} - \mathbf{E}_{10}), & (0 \leq t \leq \tau_s) \\ \mathbf{E}_{20}, & (t > \tau_s) \end{cases} \quad (40)$$

Similar to the derivative process in Section II, we can obtain the same expression for  $\mathbf{P}(t)$  as Eq.(13), except that  $F(t)$  (in the following denoted as  $G(t)$ ) is expressed as the following formulism for the special case defined in Section III,

$$G(t) = \int_t^\infty f(\tau) d\tau - \int_{t-\tau_s}^t \frac{t - \tau_s - \tau}{\tau_s} f(\tau) d\tau \quad (41)$$

Substituting the formula of  $f(\tau)$  into Eq.(41),  $G(t)$  can be expressed as

$$G(t) = \frac{B}{2\pi} \left[ \int_t^\infty \int_{-\infty}^\infty R(\omega) \exp(-i\omega\tau) d\omega d\tau - \int_{t-\tau_s}^t \frac{t - \tau_s - \tau}{\tau_s} \int_{-\infty}^\infty R(\omega) \exp(-i\omega\tau) d\omega d\tau \right] \quad (42)$$

Based on the method shown in Appendix B, Eq.(42) can be reduced to

$$G(t) = \frac{2B}{\pi} \int_0^\infty \frac{\text{Im}R(\omega)}{\omega} \frac{\sin \omega t - \sin \omega(t - \tau_s)}{\omega \tau_s} d\omega \quad (43)$$

Eqs. (34) and (43) are the basic equations used to investigate the electronic polarization process.

The frequency-dependent complex dielectric permittivity plays an important role in the study of dielectric relaxation processes. Complex dielectric permittivity can be calculated from complex refractive index. The optical constants-complex refractive index,

$n(\omega)=n'(\omega)+in''(\omega)$ , have been measured for many solvents at a nearly whole frequency range ( $\omega=0-10^{17}$  Hz). Based on the basic relationship between  $n(\omega)$  and  $\varepsilon(\omega)$ , namely,  $\varepsilon(\omega)=n^2(\omega)$ , we have

$$\begin{aligned}\varepsilon(\omega) &= \varepsilon'(\omega) + i\varepsilon''(\omega) \\ &= n'^2(\omega) - n''^2(\omega) + i2n'(\omega)n''(\omega)\end{aligned}\quad (44)$$

For an isotropic and homogeneous medium imposed by an external electric field  $\mathbf{E}_0$ , the polarization of the solvent takes the following expression by using the simple spherical approximation, *i.e.*,

$$\mathbf{P}=\chi_s\mathbf{E}=\frac{\chi_s}{\varepsilon_s}\mathbf{E}_0=\frac{\varepsilon_s-1}{4\pi\varepsilon_s}\mathbf{E}_0\quad (45)$$

Combining the relationship,  $\mathbf{P}(\omega)=R(\omega)\mathbf{E}_0(\omega)$ , we have

$$R(0)=\frac{\varepsilon_s-1}{4\pi\varepsilon_s}\quad (46)$$

For the general case, we can easily obtain the following equations,

$$\begin{aligned}R(\omega) &= \frac{\varepsilon(\omega)-1}{4\pi\varepsilon(\omega)} \\ R''(\omega) &= \frac{1}{4\pi}\frac{\varepsilon''(\omega)}{\varepsilon'^2(\omega)+\varepsilon''^2(\omega)}\end{aligned}\quad (47)$$

Substituting Eq.(47) into Eqs. (34) and (43), we have

$$\begin{aligned}F(t) &= \frac{2B}{\pi}\int_0^\infty\frac{\varepsilon''(\omega)}{\varepsilon'^2(\omega)+\varepsilon''^2(\omega)}\frac{1}{\omega}\cos\omega t d\omega \\ G(t) &= \frac{2B}{\pi}\int_0^\infty\frac{\varepsilon''(\omega)}{\varepsilon'^2(\omega)+\varepsilon''^2(\omega)}\frac{1}{\omega}\frac{\sin\omega t-\sin\omega(t-\tau_s)}{\omega\tau_s}d\omega\end{aligned}\quad (48)$$

(49)

However, the experimentally obtained optical constants are a series of discontinuous representation,  $[\omega_i, n'(\omega_i), n''(\omega_i)]$ , thus it is the same for the complex dielectric permittivity,  $[\omega_i, \varepsilon'(\omega_i), \varepsilon''(\omega_i)]$ . The integral in Eqs.(34) and (43) can be solved analytically only when we know the continuous expression for  $\varepsilon(\omega)$ . There exist some functional forms for the complex dielectric permittivity, *e.g.*, a multiple Debye, a Davision-Cole, and a Cole-Cole form [26]. However, the Debye form is not valid for the high-frequency portion of  $\varepsilon(\omega)$  and the solvation correlation function calculated from the Davision-Cole, and the Cole-Cole forms were shown to exhibit significant differences [32]. Thus, in this work, we have used linear interpolation method to deal with the experimental data to get the dielectric spectra  $\varepsilon(\omega)$ . We assume that  $g(\omega)$  can take the following form, *i.e.*,

$$g(\omega)=\frac{\varepsilon''(\omega)}{\varepsilon'^2(\omega)+\varepsilon''^2(\omega)}\frac{1}{\omega}\quad (50)$$

Then in the interval  $[\omega_i, \omega_{i+1}]$ , we have

$$\begin{aligned}g(\omega) &= \frac{\omega-\omega_i}{\omega_{i+1}-\omega_i}g_{i+1}+\frac{\omega_{i+1}-\omega}{\omega_{i+1}-\omega_i}g_i \\ &\equiv A_i g(\omega_{i+1})+B_i g(\omega_i)\end{aligned}\quad (51)$$

Substituting Eq.(51) into Eqs. (48) and (49), noticing the integral interval when  $t$  is less than  $\tau_s$ , and solving the integral analytically, we obtain

$$\begin{aligned}F(t) &= \sum_{i=1}^{N-1}\left[\frac{g_{i+1}\sin\omega_{i+1}t-g_i\sin\omega_it}{t}+\right. \\ &\quad \left.\frac{g_{i+1}-g_i}{(\omega_{i+1}-\omega_i)t^2}(\cos\omega_{i+1}t-\cos\omega_it)\right]\end{aligned}\quad (52)$$

when  $t>\tau_s$ ,

$$\begin{aligned}G(t) &= \sum_{i=1}^{N-1}\frac{1}{\tau_s}\left\{A_i\left[\int\frac{\sin(\omega t)}{(\omega t)}d(\omega t)-\right.\right. \\ &\quad \left.\left.\int\frac{\sin\omega(t-\tau_s)}{\omega(t-\tau_s)}d(\omega(t-\tau_s))\right]-\right. \\ &\quad \left.B_i\left[\frac{\cos\omega t}{t}-\frac{\cos\omega(t-\tau_s)}{(t-\tau_s)}\right]\right\}_{\omega_i}^{\omega_{i+1}}\end{aligned}\quad (53)$$

when  $t\leq\tau_s$ ,

$$\begin{aligned}G(t) &= \sum_{i=1}^{N-1}\frac{1}{\tau_s}\left\{A_i\left[\int\frac{\sin(\omega t)}{(\omega t)}d(\omega t)-\omega(t-\tau_s)\right]-\right. \\ &\quad \left.B_i\left[\frac{\cos\omega t}{t}+\frac{\omega^2(t-\tau_s)}{2}\right]\right\}_{\omega_i}^{\omega_{i+1}}\end{aligned}\quad (54)$$

We have used the complex optical and permittivity constants in nearly whole frequency range for water, methanol, and acetonitrile to calculate the dielectric response functions. The experimentally optical constants for water in nearly whole frequency range [33] are used while for methanol and acetonitrile, we have used the fitting optical constants in high frequency [34,35]. The linear variation time intervals for the external electric field are from 0 to  $5\times 10^{-6}$ ,  $5\times 10^{-5}$ ,  $5\times 10^{-4}$ ,  $5\times 10^{-3}$ , and  $5\times 10^{-2}$  ps, respectively. Figure 1 shows the time evolution of the dielectric response functions for the three solvent

When the external electric field undergoes a sudden change ( $\tau_s=0$ ) or the linear variation time intervals for the external electric field being from 0 to  $5\times 10^{-6}$ ,  $5\times 10^{-5}$  ps, we can see some common features of the dielectric response functions for the three polar solvents: when the time is under  $10^{-5}$  ps,  $F(t)\approx 1$ , which means that in such a timescale, any polarization cannot respond to such a perturbation. On the other hand, when the time is in the range  $10^{-5}-10^{-4}$  ps,  $F(t)$  falls from 1 to a minimum, the value of which is about 0.3 for water and methanol while it is zero for acetonitrile. Then  $F(t)$  undergoes a bounce-back process and a process of convergent oscillations when  $t=10^{-4}-10^{-3}$  ps. However,  $F(t)$  changes gently when  $t=10^{-3}-10^{-2}$  ps and this should belong to the time-region that the electronic polarization is completed and the orientational polarization relaxation begins. However, when the external electric field changes linearly from 0 to  $5\times 10^{-4}$ ,

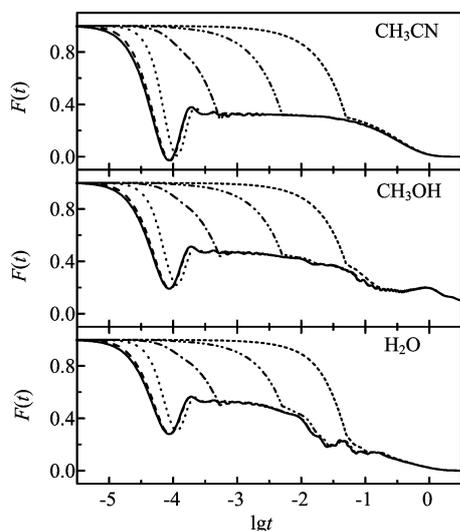


FIG. 1 Dielectric response functions for electronic polarization processes of water, methanol, and acetonitrile. The solid line represents the dielectric response function when the electrostatic field imposed on the medium undergoes a sudden change. The other five curves from left to right in order correspond to  $\tau_s=5\times 10^{-6}$ ,  $5\times 10^{-5}$ ,  $5\times 10^{-4}$ ,  $5\times 10^{-3}$ , and  $5\times 10^{-2}$  ps, respectively.

$5\times 10^{-3}$ , and  $5\times 10^{-2}$  ps, we can see that the minimum vanishes. Thus, we can confirm that the electronic transition finishes at the minima, that is,  $t_0\approx 10^{-4}$  ps. The time period of  $5\times 10^{-4}$  ps is seen to be the smallest time interval necessary for the electronic polarization. For a typical electron transfer process, the electronic transition timescale is at the scale of about femto-second, thus, here we have adopted different external electric field to represent the electronic transition process in order to investigate its effects on the solvent electronic polarization process. From Fig.1, We can conclude that the electronic polarization of the solvents will accompany the electronic transition synchronously, without time lag. And the timescale of the electronic polarization process correlates well with the vibronic frequencies in molecules [36]. Thus, we expect that further attention should be paid to the coupling between solute electronic transition and solvent electronic polarization. For different solvents, the curves of  $F(t)$  for the time evolution of electronic polarization are not the same. For the three investigated solvents, there is a process of orientational polarization, and this relates to the linear attenuation process of  $F(t)$  corresponding to the time region  $t=0.2-2$  ps.

Considering the fast electronic motion in dielectric, the electronic polarization is in general regarded to be instantaneous. Even so, it is valuable to elaborate the electronic polarization effect in chemical reactions and some ultrafast physical processes. In the present work, we have used the experimentally measured macro-physical quantity, dielectric spectra to investigate the

electronic polarization process of polar solvents based on a novel dielectric response function. For highly polar solvents, the major interactions between solvent molecules are electrostatic interaction. In fact, knowledge of the dielectric spectra, would allow for exact predictions of dynamical properties of systems, such as the dynamic Stokes shift, if the system were of macroscopic size and if only electrostatic interaction were dominant [37]. In the present work, the electronic polarization process for three polar solvents is shown in detail based on a simple continuum model. Thus, many factors that would affect the polarization process are ignored, such as the coupling between the electronic transition of the solute and the solvent electronic polarization.

The validity of linear interpolation method to the treatment of the experimentally measured dielectric permittivity can be tested by comparing with the long-wavelength dielectric function, the Debye model for the slow part of the dielectric response. The Debye model takes the slow part of the dielectric response the following form

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + i\omega\tau_D} \quad (55)$$

The dielectric response in this model is thus characterized by three parameters: the optical  $\varepsilon_\infty$  and static  $\varepsilon_s$  dielectric constants, and the Debye relaxation time  $\tau_D$ . Generally, for water, the three parameters take the values of 4.21, 78.30, and 8.2 ps for  $\varepsilon_\infty$ ,  $\varepsilon_s$ , and  $\tau_D$ , respectively. Substituting Eq.(50) into Eqs. (43), (34) and integrating analytically, we have

$$F(t) = \exp\left(-\frac{\varepsilon_s}{\varepsilon_\infty} \frac{t}{\tau_D}\right) = \exp\left(-\frac{t}{0.43}\right) \quad (56)$$

The result correlates well with the previous results [18,19]. And this confirms the validity of linear interpolation to the treatment of experimentally measured dielectric permittivity.

## V. TIME-CORRELATED POLARIZATION

Substituting Eq.(45) into Eq.(35), we obtain time-correlated response functions for polarization,

$$\mathbf{P}(t) = \frac{\varepsilon_s - 1}{4\pi\varepsilon_s} \{F(t)\mathbf{E}_{10} + [1 - F(t)]\mathbf{E}_{20}\} \quad (57)$$

The time-correlated polarization response functions for the three solvents are obtained based on the dielectric response functions calculated above. In order to qualitatively show the features of the electronic polarization, we simply assume the uniform field of  $E_{10}=1$  V/m and  $E_{20}=10$  V/m. Before  $t<10^{-6}$  ps, no response is found even if we take the sudden loading of the external electric field at  $t=0$ . The polarization response functions are shown in Fig.2.

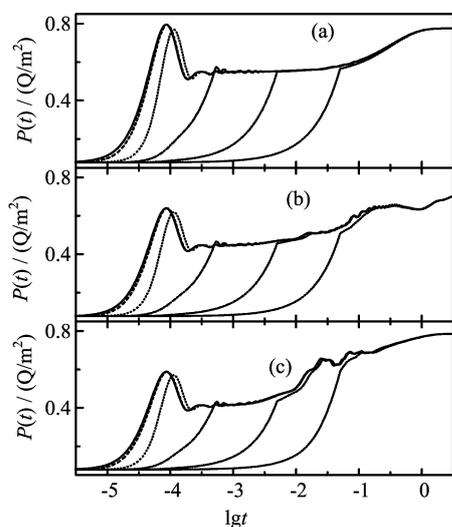


FIG. 2 Polarization response functions for water, methanol, and acetonitrile in different cases of external field loading. The thin solid line represents sudden loading ( $\tau_s=0$ ). The other five curves from left to right in order correspond to  $\tau_s=5 \times 10^{-6}$ ,  $5 \times 10^{-5}$ ,  $5 \times 10^{-4}$ ,  $5 \times 10^{-3}$ , and  $5 \times 10^{-2}$  ps, respectively.

As is shown in Fig.2, when the time is greater than 0, first is the electronic polarization which experiences a process from start to bounce-back, then to the decay oscillation, and finally to complete. Then the displacement polarization undergoes a same process like the electronic polarization. Finally is the orientational polarization in which process there exist another linear growth process towards to the final equilibrium state. When the external electric field is imposed on the solvents by linear variation with the time, we can see that the polarization processes are the same as the sudden case when the external electric field is imposed completely. However, the polarization process is somewhat different during the imposing process as can be seen from the dielectric response function.

## VI. CONCLUSION

We have presented a novel dielectric response function for dielectric relaxation process of dielectric medium. We apply the general dielectric response function to the previous implementations of continuum solvation model to the treatment of time-dependent solvation phenomena, and the results correlate well with previous expressions by using the spherical cavity approximation. The generalized response function can be used to deal with any shape and charge distribution of the solute, not limited to continuum model that the solute is limited to a cavity embedded in continuum mediums. As an application, by using the experimentally frequency-dependent dielectric permittivity, we have adopted the linear interpolation method to

deal with the discontinuous dielectric permittivity and shown the time-correlated dielectric response functions and polarization responses of three polar solvents, *e.g.*, water, methanol, and acetonitrile. We have shown the electronic polarization process for the three solvents in detail. From the results we have drawn a conclusion that the electronic polarization of the solvents will accompany the electronic transition synchronously, without time lag. For different solvents, the time needed to complete the electronic polarization is a little different. However, we should remember that through such a simple continuum model, it is hard to consider the coupling between the electronic transition of the solute and the solvent electronic polarization process, and such consideration may be resort to explicit models together with quantum mechanics. Future work is still needed and will be focused on this process more deeply and on different heterogeneous systems, where (electronic) polarization effect is important.

## VII. ACKNOWLEDGMENT

This work was supported by the National Natural Science Foundation of China (No.20533070, No.20625331, and No.20873087).

## APPENDIX A:

### On the neglect of retardation effect for solute-solvent system

For dynamic electromagnetic field, there exists the retardation effect for the influence of the field source on the field. The retarded potential can be written as [21]

$$\varphi(\mathbf{r}, t) = \int_{V'} \frac{\rho(\mathbf{r}', t - R/c)}{R} dV' \approx \int_{V'} \frac{\rho(\mathbf{r}', t)}{R} dV' \quad (\text{A1})$$

in which  $t' = t - R/c$ ,  $R = |\mathbf{r} - \mathbf{r}'|$ , and  $c$  is the speed of light. Based on the formalism, we can see that the source charge  $\rho(\mathbf{r}', t')$  would influence the field  $\mathbf{E}(\mathbf{r}, t' + R/c)$  after a short time  $\Delta t = R/c$ . Then we can estimate the retardation time for the influence of solute charge distribution on the solvent polarization. We assume that the radius of the solute molecule is about 1.5–30 Å, and the range of the surrounding solvent molecules affected by the solute molecule is ten times as the radius of the solute molecule, namely,  $R = 15\text{--}300$  Å. Then the retardation time  $\Delta t = R/c = 0.5 \times 10^{-5}\text{--}10 \times 10^{-5}$  ps which means the retardation time is less than the characteristic time ( $10^{-4}$  ps, evaluated from the vibronic frequency) of the electronic polarization. Thus we can expect that to deal with the electromagnetic field of the solute-solvent system as electrostatic field would not induce apparent errors.

## APPENDIX B: Proof of Eq.(32)

The integral part in Eq.(31) can be rewritten as

$$\int_{-\infty}^{\infty} \int_t^{\infty} d\tau R(\omega) \exp(-i\omega\tau) d\omega$$

$$\begin{aligned}
&= \int_{-\infty}^{\infty} R(\omega) \frac{\exp(-i\omega\tau)}{-i\omega} \Big|_{\tau=t}^{\tau \rightarrow \infty} d\omega \\
&= \int_{-\infty}^{\infty} (R' + iR'') \frac{\cos \omega t - i \sin \omega t}{-i\omega} \Big|_{\tau=t}^{\tau \rightarrow \infty} d\omega \\
&= \int_{-\infty}^{\infty} \frac{(R_0 - R') \sin \omega t + R'' \cos \omega t}{\omega} d\omega - \\
&\quad \int_{-\infty}^{\infty} \frac{(R_0 - R') \sin \omega \tau + R'' \cos \omega \tau}{\omega} d\omega - \\
&\quad \int_{-\infty}^{\infty} \frac{R_0 \sin \omega t}{\omega} d\omega + \int_{-\infty}^{\infty} \frac{R_0 \sin \omega \tau}{\omega} d\omega \quad (B1)
\end{aligned}$$

for  $R_0 = R(\omega)|_{\omega \rightarrow 0}$  and  $\tau \rightarrow \infty$ ,

$$-\int_0^{\infty} \frac{\sin \omega t}{\omega} d\omega + \int_0^{\infty} \frac{\sin \omega \tau}{\omega} d\omega = 0 \quad (B2)$$

Since both  $\frac{R_0 - R'}{\omega} \Big|_{\omega \rightarrow 0}^{\omega \rightarrow \infty}$  and  $\frac{R''}{\omega} \Big|_{\omega \rightarrow 0}^{\omega \rightarrow \infty}$  are finite values, so when  $\tau$  goes to infinity,

$$\int_{-\infty}^{\infty} \frac{(R_0 - R') \sin \omega \tau}{\omega} d\omega = \int_{-\infty}^{\infty} \frac{R'' \cos \omega \tau}{\omega} d\omega \equiv 0 \quad (B3)$$

Thus, Eq.(B1) changes into the following form,

$$\begin{aligned}
&\int_{-\infty}^{\infty} \int_t^{\infty} R(\omega) \exp(-i\omega\tau) d\omega d\tau \\
&= 2 \int_0^{\infty} \frac{(R_0 - R') \sin \omega t + R'' \cos \omega t}{\omega} d\omega \\
&\equiv 2 \int_0^{\infty} \frac{[R(\omega) - R_0] \exp(-i\omega t)}{i\omega} d\omega \quad (B4)
\end{aligned}$$

When  $t$  is greater than 0, by applying a procedure originally developed by Hsu *et al.* [9], we have

$$\int_0^{\infty} \frac{(R_0 - R') \sin \omega t}{\omega} d\omega \equiv \int_0^{\infty} \frac{R'' \cos \omega t}{\omega} d\omega \quad (B5)$$

Combining Eqs. (B4) and (B5), we can obtain Eq.(32),

$$\begin{aligned}
F(\mathbf{r}, t) &= \frac{B}{2\pi} \int_t^{\infty} \int_{-\infty}^{\infty} R(\mathbf{r}, \omega) \exp(-i\omega\tau) d\omega d\tau \\
&= \frac{2B}{\pi} \int_0^{\infty} \frac{R''(\mathbf{r}, \omega)}{\omega} \cos \omega t d\omega \quad (B6)
\end{aligned}$$

In the above proof process, we have used  $R'$  and  $R''$  indicating the real and imaginary part of  $R_j(\mathbf{r}, \omega)$ , respectively.

- [1] R. Jimenez, G. R. Fleming, P. V. Kumar, and M. Maroncelli, *Nature* **369**, 471 (1994).
- [2] M. L. Horng, J. A. Gardecki, A. Papazyan, and M. Maroncelli, *J. Phys. Chem.* **99**, 17311 (1995).
- [3] B. M. Ladanyi and R. M. Stratt, *J. Phys. Chem.* **100**, 1266 (1996).
- [4] Y. Chen, R. X. Xu, H. W. Ke, and Y. J. Yan, *Chin. J. Chem. Phys.* **20**, 438 (2007).
- [5] B. Bagchi, *Annu. Rev. Phys. Chem.* **115**, 40 (1989).

- [6] G. R. Fleming and M. Cho, *Annu. Rev. Phys. Chem.* **109**, 47 (1996).
- [7] N. Nandi, K. Bhattacharyya, and B. Bagchi, *Chem. Rev.* **100**, 2013 (2000).
- [8] D. F. Parsons, M. V. Vener, and M. V. Basilevsky, *J. Phys. Chem. A* **103**, 1171 (1999).
- [9] D. V. Matyushov, *J. Chem. Phys.* **122**, 044502 (2005).
- [10] E. A. Carter and J. T. Hynes, *J. Chem. Phys.* **94**, 5961 (1991).
- [11] X. Y. Song, D. Chandler, and R. A. Marcus, *J. Phys. Chem.* **100**, 11954 (1996).
- [12] C. P. Hsu, X. Y. Song, and R. A. Marcus, *J. Phys. Chem. B* **101**, 2546 (1997).
- [13] X. Y. Song and D. Chandler, *J. Chem. Phys.* **108**, 2594 (1998).
- [14] M. D. Newton and H. L. Friedman, *J. Chem. Phys.* **88**, 4460 (1988).
- [15] L. E. Fried and S. Mukamel, *J. Chem. Phys.* **99**, 932 (1990).
- [16] G. P. Wolynes, *J. Chem. Phys.* **86**, 5133 (1987).
- [17] F. Ingrosso, B. Mennucci, and J. Tomasi, *J. Mol. Liq.* **108**, 21 (2003).
- [18] M. Caricato, F. Ingrosso, B. Mennucci, and J. Tomasi, *J. Chem. Phys.* **122**, 154501 (2005).
- [19] B. Mennucci, *Theor. Chem. Acc.* **116**, 31 (2006).
- [20] M. Caricato, B. Mennucci, and J. Tomasi, *J. Chem. Phys.* **124**, 124520 (2006).
- [21] L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media*, 2nd edn., New York: Pergamon, (1984).
- [22] S. Mukamel, *Principles of Nonlinear Optical Spectroscopy*. New York: Oxford University Press, (1995).
- [23] A. A. Zharikov and S. F. Fischer, *J. Chem. Phys.* **124**, 054506 (2006).
- [24] J. Tomasi, B. Mennucci, and R. Cammi, *Chem. Rev.* **105**, 2999 (2005).
- [25] B. Bagchi, D. W. Oxtoby, and G. R. Fleming, *Chem. Phys.* **86**, 257 (1984).
- [26] C. J. F. Bottcher and P. Bordewijk, *Theory of Electric Polarization*, Vol. 2, Amsterdam: Elsevier, (1978).
- [27] R. A. Marcus, *J. Phys. Chem.* **96**, 1753 (1992).
- [28] M. Marchi, J. N. Gehlen, D. Chandler, and M. D. Newton, *J. Am. Chem. Soc.* **115**, 4178 (1993).
- [29] H. J. Kim and J. T. Hynes, *J. Phys. Chem.* **94**, 2736 (1990).
- [30] J. N. Gehlen, D. Chandler, H. J. Kim, and J. T. Hynes, *J. Phys. Chem.* **96**, 1748 (1992).
- [31] H. J. Kim and J. T. Hynes, *J. Chem. Phys.* **96**, 5088 (1992).
- [32] M. Maroncelli, E. W. Jr. Castner, B. Bagchi, and G. R. Fleming, *Faraday Discuss. Chem. Soc.* **85**, 199 (1988).
- [33] D. Segelstein and M. S. Dissertation. *The Complex Refractive Index of Water*, Kansas: University of Missouri-Kansas City, (1981).
- [34] K. Y. Bang, S. Lee, H. Oh, I. An, and H. Lee, *Bull. Korean Chem. Soc.* **26**, 947 (2005).
- [35] B. Kong, K. X. Fu, M. H. Shan, and X. Y. Li, *Chin. J. Chem. Phys.* **22**, 262 (2009).
- [36] J. L. McHale, *Molecular Spectroscopy*, Upper Saddle River, New Jersey: Prentice Hall, (1999).
- [37] R. M. Stratt and M. Maroncelli, *J. Phys. Chem.* **100**, 12981 (1996).