Dielectric friction and the transition from adiabatic to nonadiabatic electron transfer in condensed phases. II. Application to non-Debye solvents

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Outer sphere electron transfer rates in polar media are analyzed for non-Debye solvents whose dielectric function contains a few relaxation times (e.g., linear alcohols) or has a continuous distribution of relaxation times (e.g., the Cole-Davidson form for glycerol). The activation free energy and the preexponential factor are calculated and related to the solvent polarity and dielectric relaxation. The conditions for observing a fractional power dependence of the rate on the solvent time scale are analyzed.

I. ELECTRON TRANSFER RATES IN POLAR SOLVENTS

In part I of this series, we derived a new expression for outer sphere electron transfer (ET) rates in polar solvents, whose dielectric function \( \epsilon(\omega) \) has the general form

\[
e(\omega) = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty) \chi(\omega).
\]

Here \( \epsilon_0 \) is the static (\( \omega = 0 \)) and \( \epsilon_\infty \) is the high frequency (optical) value of \( \epsilon(\omega) \), and the frequency dependence \( \chi(\omega) \) reflects the dynamical dielectric relaxation of the solvent. Detailed analysis and numerical calculations were performed for the Debye model in which the dielectric function is characterized by a single relaxation time. In this article, we analyze the ET rate and its dependence on the solvent properties for typical non-Debye solvents. The model for ET considered in I consists of the charge transfer system which has two states corresponding to the electron on the donor or the acceptor site and denoted \( |a\rangle \) and \( |b\rangle \), respectively. The system is interacting electrostatically with a polar solvent. The electric field at position \( r \), created by the system in states \( |a\rangle \) and \( |b\rangle \), is denoted \( D_a(r) \) and \( D_b(r) \), respectively. The exothermicity of the reaction is denoted by \( E \). It includes the interaction energy with the solvent electronic degrees of freedom, which are assumed to respond instantaneously to the charge rearrangements in the system. The states \( |a\rangle \) and \( |b\rangle \) are coupled by a nonadiabatic electronic matrix element \( V \) (Fig. 1). The ET rate derived in I is

\[
K = \frac{2\pi(V^2/\hbar) \sigma(\delta_a - E)}{1 + \sqrt{2\pi(V^2/\Delta\hbar)} \left[ \tau(q_a) + \tau(q_b) \right]}. 
\]

In this expression, \( \sigma(x) \) is an ordinary absorption line shape function, given by

\[
\sigma(x) = \frac{1}{\pi\hbar} \text{Re} \int_0^\infty dt \exp \left[ ixt/\hbar - g(t) \right]
\]

with

\[
g(t) = (\Delta/\hbar)^2 \int_0^t \int_0^\tau_1 d\tau_1 d\tau_2 M(\tau_2).
\]

Here

\[
M(t) = Q(t)/Q(0),
\]

with

\[
Q(t) = \frac{i}{2\pi} \int_{-\infty}^\infty \frac{d\omega}{\omega} \exp(-i\omega t) \left[ \frac{1}{\epsilon(\omega)} - \frac{1}{\epsilon_0} \right],
\]

and \( Q(0) \) is equal to the Pekar factor

\[
Q(0) = 1/\epsilon_\infty - 1/\epsilon_0.
\]

We further have

\[
\Delta^2 = \left[ k_b T \left| \Gamma_a - \Gamma_b / 4\pi \right| (1/\epsilon_\infty - 1/\epsilon_0) \right],
\]

\[
\delta_m = (\Gamma_m/4\pi) (1/\epsilon_\infty - 1/\epsilon_0), \quad m = a, b
\]

and

\[
\Gamma_m = \int dr \left[ D_a(r) - D_b(r) \right] \cdot D_m(r).
\]

The solvent time scale function is given by

\[
\tau(q_m) = \exp \left[ \frac{-q_m^2}{2} \right] \int_0^\infty dt \frac{1}{\sqrt{1 - M^2(t)}}
\]

\[
\times \exp \left[ \frac{q_m^2 M(t)}{1 + M(t)} - 1 \right], \quad m = a, b
\]

with

\[
q_m^2 = \frac{(E - \delta_m^2)}{k_b T |\delta_a - \delta_b|}, \quad m = a, b.
\]

Equation (1.2), together with Eqs. (1.3)–(1.12), were derived in I. They provide a closed expression for the ET rate and relate it to properties of the ET system and to the solvent dielectric function. It should be noted that in Eq. (1.2) we have assumed that the donor and the acceptor harmonic potentials have the same frequency. This is a consequence of the perturbative treatment of the interaction between the system and the solvent. The formalism developed in I and Eq. (4.7) of Ref. 1 is not restricted, however, to this limiting case. A Liouville-space formulation of optical line shapes, which allows for different harmonic frequencies, has been developed and may be used to generalize Eq. (1.2).

The adiabatic character of the ET process is controlled by the adiabaticity parameter

\[
\nu = \sqrt{2\pi(V^2/\Delta\hbar)} \left[ \tau(q_a) + \tau(q_b) \right].
\]
When \( \nu \ll 1 \), the rate process is nonadiabatic:

\[
K_{\text{NA}} = 2\pi(V^2/\hbar)\sigma(\delta_a - E), \quad \nu \ll 1,
\]

whereas when \( \nu \gg 1 \), it is adiabatic

\[
K_A = (2\pi\Delta^2)^{1/2}\sigma(\delta_a - E)/(\tau(q_a) + \tau(q_b)), \quad \nu \gg 1.
\]

When \( \hbar/\Delta \) is much smaller than all solvent time scales relevant for the ET, Eq. (1.3) assumes the form

\[
\sigma(x) = (2\pi\Delta^2)^{-1/2}\exp(-x^2/2\Delta^2).
\]

This is the static limit of the theory of spectral line shapes and it is always attained at sufficiently high temperatures [see Eq. (1.8)]. In this limit, the rate [Eq. (1.2)] can be written in an activated form

\[
K = A \exp(-\Delta G^*_{\text{ab}}/k_B T),
\]

where the activation free energy is

\[
\Delta G^*_{\text{ab}} = \frac{(E - \delta_a)^2}{2|\delta_a - \delta_b|},
\]

and the preexponential factor is

\[
A = \frac{(2\pi)^{1/2}(V^2/\Delta \hbar)}{1 + (2\pi)^{1/2}(V^2/\Delta \hbar)(\tau(q_a) + \tau(q_b))}. \tag{1.19}
\]

Let us briefly comment on the significance of these quantities. The solvent dynamics are contained in \( M(t) \), which is the normalized correlation function of the reaction coordinate. \( M(t) \) enters Eq. (1.2) via the line shape function \( \sigma(x) \) and through the function \( \tau(q_m) \) [Eq. (1.11)], which is a characteristic relaxation time for solvent fluctuations, when the reaction coordinate is perturbed around the value \( E - \delta_m \), \( \tau(q_m) \) represents the solvent time scale relevant for the ET rate. In the static limit, which often holds in ET reactions \( \sigma(x) \) becomes independent of the solvent time scale [see Eq. (1.16)], and the only dependence on solvent dynamics is then contained in \( \tau(q_m) \). All other quantities appearing in Eq. (1.2) (\( \Delta, \delta_a, \text{and} \delta_b \)) depend on the Pekar factor which is related to the solvent polarity but not to its dynamics. \( \delta_m \) is the expectation value of the reaction coordinate, when the molecule is in the state \( |m\rangle \) (\( m = \delta_a, \delta_b \)). One of the important conclusions from Eq. (1.18) together with Eq. (1.9) is that the activation free energy depends on the solvent only through the Pekar factor. The solvent dynamics do not affect \( \Delta G^*_{\text{ab}} \). In particular for \( E = 0 \) we have

\[
\Delta G^*_{\text{ab}} = \left( \Gamma^2 / (8\pi |\Gamma_a - \Gamma_b|) \right) (1/\epsilon_a - 1/\epsilon_b). \tag{1.20}
\]

Marcus\(^5\) has derived this relation for Debye solvents. The present theory shows that this result is valid for an arbitrary non-Debye solvent as well. \( \Gamma_m \) depend on the charge distribution of the ET system and are approximately independent of the solvent.

The solvent time scale function \( \tau(q_m) \) plays a key role in the present theory. It is important, therefore, to define the conditions whereby the integration in Eq. (1.11) converges. If \( M(t) \) decays at long times, faster than \( \sim 1/t \), and if it starts at short times as

\[
M(t) = 1 - t^\alpha, \quad t \to 0 \tag{1.21}
\]

with \( \alpha < 2 \), then the integral converges, and \( \tau(q_m) \) is finite. These conditions are usually satisfied for realistic solvents with one of the standard forms of \( \epsilon(\omega) \), as will be demonstrated in this article. Our expression for the ET rate [Eq. (1.2)] unifies and generalizes the existing theories of outer sphere electron transfer. The nonadiabatic rate expression [Eq. (1.14)] was developed by Levich and co-workers\(^{10,11}\) for Debye solvents and then generalized to an arbitrary solvent by Ovchinnikov and Ovchinnikova\(^11\) and by Zusman and Helman.\(^12\) The nonadiabatic limit of Eq. (1.2), as given in Eq. (1.14), is identical to Eq. (26a) of Ref. 11. Zusman\(^14\) obtained an expression for the ET rate that is nonperturbative in \( V \). His formulation is restricted to the Debye model and to high temperatures. Under these circumstances, we have shown in I that our rate expression (1.2) is equal to Eq. (29) of Ref. 14(a). Marcus\(^5\) considered the effects of solvation on the activation free energy. Using a Debye model for the solvent, he showed that the activation free energy [Eq. (1.18)] is related to the Pekar factor [Eq. (1.18), together with Eq. (1.9)]. The present derivation shows that this result is valid for an arbitrary (non-Debye) solvent as well. Sumi and Marcus,\(^15\) using an adiabatic formulation of the rate process, argued that the dielectric function of linear alcohols, which has three different relaxation times, can be reduced to an equivalent Debye model. In this form, the rate expressions valid for Debye solvents can be used. They obtained an expression for activationless ET rate with an adiabatic model for Debye solvents. It was shown in I that \( \tau_a \), defined in Eq. (9.1) of Ref. 15, can be obtained from our Eq. (1.15) by neglecting the effects of back reaction. Recently, Rips and Jortner\(^16\) used a path integral formulation to get a formula for the ET rate for Debye solvents. With a similar argument as Sumi's and Marcus's, they also addressed the issue of the ET in alcohols, reducing the solvent dynamics to an equivalent Debye model. They obtained a rate expression valid for the Debye model at high temperatures. If we use our expression (1.2) for the rate under these conditions, neglecting the effect of the back reaction, i.e., \( \tau(q_a) \gg \tau(q_b) \),
and using the static limit expression for $\sigma(x)$, Eq. (1.16), we obtain Eq. (3.32) of Ref. 16. Hynes\textsuperscript{17} derived a formula for the rate based on an adiabatic description of the ET reaction. He used a Smoluchowsky equation for non-Markovian processes to describe the reaction coordinate probability distribution. He then expressed the rate in terms of the dielectric function of the solvent $\epsilon(\omega)$. This result, however, neglects the effects of the back reaction that, as shown by numerical simulations\textsuperscript{18} and by our previous analysis in I, may overestimate the actual reaction rate. If we use the adiabatic limit Eq. (1.15), neglect the effect of the back reaction, and use the static limit for $\sigma(x)$ [Eq. (1.16)], we obtain Eq. (3.10) of Ref. 17.

In Secs. II and III, we shall apply our results to calculate the ET rate for solvents which belong to two classes of models for dielectric relaxation. The first class considered in Sec. II consists of solvents, whose dielectric function is characterized by a weighted linear combination of a few ($N$) Debye functions. These solvents have, therefore, $N$ relaxation times. Typical examples for this class are alcohols\textsuperscript{2-19} which have $N = 3$. Solvents belonging to the second class are characterized by a continuous distribution of relaxation time scales, and their dielectric function can be written in terms of the dimensionless quantity $\sigma \tau_0$, where $\tau_0$ is a scaling parameter. The most common forms used in this class are the Cole–Cole, the Cole–Davidson, and the Williams–Watts dielectric functions.\textsuperscript{3} The Debye model is a limiting case of both classes. In Sec. III, we consider the Cole–Davidson model as an example for solvents belonging to the second class. Finally in Sec. IV, we summarize the implications of the present theory.

II. APPLICATION TO SOLVENTS WITH A FEW RELAXATION TIMES: LINEAR ALCOHOLS

In this section, we analyze our rate expression Eq. (1.2) for solvents with a few relaxation times characterized by the following dielectric function\textsuperscript{3}

$$\epsilon(\omega) = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty) \sum_{j=1}^{N} \frac{g_j}{1 - i\omega \tau_j},$$

(2.1)

Using Eqs. (1.5), (1.6), and (2.1), we can express $M(t)$ in the form

$$M(t) = \sum_{j=1}^{N} c_j \exp(-t/\tau_j),$$

(2.2)

where the coefficients $c_j$ and the characteristic times $\tau_j$ can be expressed in terms of $\epsilon_\infty$, $\epsilon_0$, $g_j$, and $\tau_j$ by solving the roots for an $N$th order polynomial. Note that $\Sigma c_j \tau_j = \Sigma g_j = 1$. Equation (2.2) shows that the relevant solvent time scales for ET are $\tau_j$ and not $\tau_j$ [Eq. (2.1)]. The Debye dielectric function is given by Eq. (2.1) with $N = 1$. We will denote here and throughout this paper the Debye relaxation time scale [i.e., $\tau_1$ of Eq. (2.1) for $N = 1$] by $\tau_D$. For the Debye model, we have

$$\tau_1 = \tau_L = \tau_D (\epsilon_\infty / \epsilon_0),$$

(2.3)

where $\tau_L$ denotes the solvent longitudinal relaxation time. For solvents with two relaxation times ($N = 2$), we have

$$2/\tau_j = 1/\tau^{*} \pm \left[1/\tau^{*2} - 4(\epsilon_0/\epsilon_\infty)(\tau_1\tau_2)^{-1}\right]^{1/2},$$

(2.4a)

where the + and − signs correspond to $\tau_1$ and $\tau_2$, respectively, and where

$$1/\tau^{*} = (1/\tau_1) [g_1(\epsilon_0/\epsilon_\infty - 1) + 1] + (1/\tau_2) [g_2(\epsilon_0/\epsilon_\infty - 1) + 1].$$

(2.4b)

When $g_j \ll g_1$, we get

$$\tau_1 \approx (\epsilon_\infty / \epsilon_0) \tau_1,$$

(2.5a)

$$\tau_2 \approx \tau_2.$$  

(2.5b)

An example for a model solvent with two relaxation times is provided by the microscopic model of rotational diffusion with intermolecular forces developed by Berne.\textsuperscript{18b}

Equation (2.5) can be easily generalized to solvents with $N$ relaxation times. If one $g_j$ is dominant (say $g_1 > g_j \neq 1$), then $\tau_j$ will be given by Eq. (2.5a), and the other $\tau_j$ ($j \neq 1$) will be approximately given by Eq. (2.5b). Equations (2.4) illustrate that, in general, we cannot obtain $\tau_f$ from $\tau_j$ by simply multiplying with $(\epsilon_\infty / \epsilon_0)$, as is the case for the Debye model.

We have calculated $M(t)$ and the ET rate for linear alcohols (propanol to decanol). These solvents have three relaxation times ($N = 3$). We have used the values of $\tau_j$ and $g_j$ at 20°C, as reported by Garg and Smyth.\textsuperscript{19} In Table I, we give $g_j$, $\tau_j$, and $\tau_j$ calculated numerically. An examination of these numbers shows that in all cases $g_1 \gg g_2$, $g_3$. This may lead to the conclusion that mode 1 (with the relaxation time $\tau_1$) is the dominant time scale. This conclusion is, however, misleading. As is clear from our analysis, the solvent time scales relevant for ET are $\tau_j$ and their relative weights are $c_j$. The values of $c_j$, given in Table I, show that, although $g_1 \gg g_2$, $g_3$, this is not true for $c_j$ and $c_1$, $c_2$, and $c_3$ are not that different. Therefore, all three modes contribute significantly to the ET process.

| Table I. Solvent dynamics and polarity parameters for the n-alcohols, studied by Kosower and Huppert (Ref. 16). $g_j$, $\tau_j$, $\epsilon_0$, and $\epsilon_\infty$ are taken from Ref. 19 at 20°C. $c_j$ and $\tau_j$ [Eq. (2.6)] were calculated numerically using Eqs. (1.4)–(1.6). A numerical calculation of the solvent time scale function $q(\tau)$ resulted in the limiting values $r(0)$ and $r(2)$ [Eq. (2.16)], which are tabulated as well. $\tau_j$, $\tau_0$, $\tau_f$, and $\tau$ are given in picoseconds. |
|---|---|---|---|---|---|---|
| Propanol | Butanol | Pentanol | Hexanol | Heptanol | Octanol | Decanol |
| $\epsilon_0$ | 20.1 | 17.1 | 13.9 | 13.2 | 11.6 | 10.2 | 8.1 |
| $\epsilon_\infty$ | 1.92 | 1.95 | 1.98 | 2.02 | 2.03 | 2.04 | 2.06 |
| $g_1$ | 0.91 | 0.90 | 0.89 | 0.89 | 0.88 | 0.85 | 0.85 |
| $g_2$ | 0.04 | 0.05 | 0.05 | 0.05 | 0.06 | 0.06 | 0.08 |
| $g_3$ | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.07 |
| $\pi_1$ | 0.41 | 0.46 | 0.52 | 0.54 | 0.56 | 0.59 | 0.59 |
| $\pi_2$ | 0.21 | 0.23 | 0.20 | 0.18 | 0.18 | 0.18 | 0.18 |
| $\pi_3$ | 0.28 | 0.31 | 0.30 | 0.28 | 0.26 | 0.23 | 0.23 |
| $\tau_1$ | 430 | 668 | 927 | 1210 | 1465 | 1780 | 2019 |
| $\tau_2$ | 21.9 | 27.6 | 31 | 34.4 | 38.7 | 47.5 | |
| $\tau_3$ | 2.5 | 2.65 | 2.9 | 3.18 | 3.23 | 3.87 | |
| $\tau_1$ | 82.1 | 140 | 219 | 299 | 398 | 526 | 733 |
| $\tau_2$ | 16.3 | 20 | 22 | 25 | 28 | 32 | 40 |
| $\pi(0)$ | 6.49 | 12.2 | 21.4 | 29.6 | 41.7 | 61.1 | 85.4 |
| $\pi$ | 0.043 | 0.058 | 0.073 | 0.078 | 0.095 | 0.12 | 0.15 |

We shall start the analysis of the ET rate by considering the nonadiabatic limit [Eq. (1.14)]. To obtain the line shape \( \sigma(x) \), we need to perform the time integration in Eq. (1.3). We first calculate \( g(t) \) using Eqs. (1.4) and (2.2),

\[
g(t) = \frac{(\Delta/\hbar)^2}{\gamma/\hbar} \sum_{j=1}^{\infty} c_j \tau_j^2 \left[ \exp\left(-\frac{t}{\tau_j}\right) - 1 + \frac{t}{\tau_j} \right].
\]

(2.6)

It will be useful to analyze \( g(t) \) in the limits of short and long times in terms of the parameters of \( \epsilon(\omega) \). This can be accomplished by starting with the Laplace transform of \( g(t) \), \( \tilde{g}(s) \), which is given by Eq. (A6), together with Eqs. (A4), (A5), and (A7). The short time behavior of \( g(t) \) can be obtained by expanding \( \tilde{g}(s) \) in powers of \( 1/s \) for large \( s \) and using Eq. (A9). The long time limit is obtained by expanding \( \tilde{g}(s) \) in a power series in \( s \) for small \( s \) and using Eq. (A11). The resulting limiting behavior is

\[
g(t) = \begin{cases} \frac{(\Delta^2/\hbar^2)}{2\gamma} \left[ 1 - at + bt^2 + \cdots \right], & t \ll t_0, \\ \left(\gamma/\hbar\right)(t - t_0), & t \gg t_0, \end{cases}
\]

(2.7)

where

\[
a = \frac{1}{2}(\epsilon_\infty/\epsilon_0)(\tau^{-1}),
\]

(2.8a)

\[
b = \frac{1}{2}(\epsilon_\infty/\epsilon_0) \left[ (\tau^{-2}) + (\epsilon_0/\epsilon_\infty - 1)(\tau^{-1})^2 \right],
\]

(2.8b)

and

\[
\gamma = \frac{1}{\hbar} \left( \epsilon_\infty/\epsilon_0 \right) \Delta^2 \langle \tau \rangle,
\]

(2.9a)

\[
t_0 = \left[ \left( \tau^2 \right) - \left( 1 - \epsilon_0/\epsilon_\infty \right) \langle \tau \rangle^2 \right]/\langle \tau \rangle.
\]

(2.9b)

In Eqs. (2.8) and (2.9), we have introduced the moments of \( \tau \), i.e.,

\[
\langle \tau^n \rangle \equiv \sum_j \gamma_j^\alpha, \quad n = 0, 1, \pm 2, \ldots.
\]

(2.10)

The moments of \( M(t) \) may be obtained by using Eq. (A5), together with Eqs. (A4), (A7), and (A12). The zeroth moment is given by

\[
\tau_M \equiv \int_0^\infty dt \, M(t) = \left( \epsilon_\infty/\epsilon_0 \right) \langle \tau \rangle.
\]

(2.11)

Note that

\[
\gamma = \frac{1}{\hbar} \Delta^2 \tau_M.
\]

(2.12)

The asymptotic short time and the long time behaviors of \( g(t) \) are identical to those of a Debye solvent.1 The behavior of the line shape in the center and in the far wings will, therefore, be the same.1,3,7,8,20 When \( x < \hbar/\tau \), for all \( j \), we have

\[
\sigma(x) = \frac{\gamma/\pi}{x^2 + \gamma^2},
\]

(2.13)

whereas when \( x > \hbar/\tau \), for all \( j \), we have

\[
\sigma(x) = (2\pi\Delta)^{-1/2} \exp\left(-\frac{x^2}{2\Delta^2}\right).
\]

(2.14)

The line shape function \( \sigma(x) \) will always be Lorentzian near the center and becomes Gaussian in the line wings. The nature of the line shape function depends on the dimensionless parameter1,8,20

\[
\kappa^{-1} = \gamma/\Delta = \sqrt{(k_B T/\hbar^2)\left|\delta_\epsilon - \delta_p\right|} \tau_M.
\]

(2.15)

If \( \kappa \gg 1 \), the line shape will be Lorentzian, around \( x = 0 \) for many linewidths, whereas when \( \kappa \ll 1 \), the onset of the Gaussian behavior occurs near the line center. Similar results were obtained earlier1,2 for the Debye model. The static limit line shape [Eq. (2.14)], which does not depend on solvent dynamics, is, of course, the same for the Debye model. In the other extreme, the line shape is given by Eq. (2.13), together with Eq. (2.9), where the \( \langle \tau \rangle \) factor in Eq. (2.9a) is replaced for the Debye model by the longitudinal time scale \( \tau_\rho \). In Fig. 2(a), we present the line shape function \( \sigma(x) \) for propenol and pentanol at 20 °C, calculated using Eqs. (1.3) and (2.6) and the data of Table I. The dashed line shows for comparison the line shape for a Debye solvent with \( \tau_\rho \) equal to \( \tau_1 \) of propenol and the same \( \epsilon_0 \) and \( \epsilon_\infty \) as propenol. The same curves are plotted in Fig. 2(b) on a logarithmic scale, where the behavior in the line wings is emphasized. These line shapes are distinctly different from the Debye line shape, even though \( g_1 > g_2, g_3 \). In Figs. 3(a) and 3(b), we show the line shape \( \sigma(x) \) for propenol for different values of \( \Delta \). For small values of \( \kappa \) (larger \( \Delta \)), the line shape is Gaussian, and \( \sigma(x) \) is independent of the solvent relaxation mechanism. As \( \kappa \) increases, \( \sigma(x) \) assumes a Lorentzian form.
The above analysis of $\sigma(x)$ corresponds to the nonadiabatic rate expression, Eq. (1.14). We shall consider now the transition to the adiabatic regime. According to Eq. (1.2), the transition will be controlled by the adiabaticity parameter $\nu$, Eq. (1.13), which depends on the solvent time scale function $\tau(q)$. We have calculated $\tau(q)$ for the linear alcohols by numerically integrating Eq. (1.11). We find the scaled solvent time scale function $\tau(q)/\tau(0)$ to be very similar for all the $n$-alcohols considered (propanol to decanol). In Fig. 4, we display $\tau(q)/\tau(0)$ for propanol (solid curve), and hexanol (dotted curve). For comparison, we also present in Fig. 4 the function $\tau(q)/\tau(0)$ for a Debye solvent (dashed line). The values of $\tau(0)$ for the alcohols are given in Table I. Note that for a Debye solvent, $\tau(0) = (\ln 2)\tau_L$. By asymptotic analysis, it can be shown that for large $q$, $\tau(q)$ varies as $~q^{-1}$. We thus have

$$\tau(q) = (2\pi)^{1/2}/q, \quad q > 5. \quad (2.16)$$

This behavior is verified in the curves given in Fig. 4. The values of $\tau_L$ for the $n$-alcohols are given in Table I. The adiabaticity parameter [Eq. (1.13)] thus assumes the form

$$\nu = \frac{2\sqrt{2\pi V^2}}{\bar{\alpha}[k_B T |\delta_a - \delta_b|]^{1/2}} \tau(0), \quad \frac{q_a q_b \ll 1}{q_a q_b \gg 1} \quad (2.17)$$

The adiabaticity parameter for large barriers depends on the electronic coupling $V$, the molecule–solvent interaction through $|E - \delta_a|$ and $|E - \delta_b|$ and on the solvent relaxation process through $\bar{\alpha}$. For the Debye model $\tau = \tau_L$ [Eq. (2.3)] and the solvent relaxation time scale that controls the transition from a nonadiabatic to an adiabatic rate for large $q$ is given by the longitudinal solvent relaxation time. In the adiabatic ($\nu \gg 1$) and static limit, the rate assumes the activated form [Eq. (1.17)] and the preexponential factor is given by

$$A = \frac{1}{2\tau(0)} \frac{1}{[2\pi k_B T |\delta_a - \delta_b|]^{-1/2} \left[|E - \delta_a|^{-1} + |E - \delta_b|^{-1}\right]^{-1} 1/\bar{\alpha}} \quad \frac{q_a q_b \ll 1}{q_a q_b \gg 1} \quad (2.18)$$

In either limit, this factor is inversely proportional to a solvent time scale [whether \( \tau_0 \) or \( \tau \)]. An interesting issue is, whether it is possible to approximately map a given alcohol to a Debye model. This can be done by introducing a mean solvent time scale \( \tau_M \) [Eq. (2.11)] and taking a Debye model with \( \tau_M = \tau_\ell \). An argument could be made that since \( g_{22} \gg g_{23}, \ g_{23} \), then \( \tau_\ell \) should be the dominant relaxation time scale, and the alcohol can be represented by a Debye model with \( \tau = \tau_\ell \). This is not the case, as can be seen from the data reported in Table 1, which show that \( \tau \) differ considerably from \( \tau_\ell \) and from \( (\varepsilon_\infty / \varepsilon_0) \tau_1 \).

One of the primary goals of any theory of ET is to predict the variation of the ET rate with solvent within a given family (e.g., alcohols, nitriles, etc.).\(^{21,22}\) A major problem in analyzing such data results from the fact that it is virtually impossible to vary one solvent property at a time, and the combined effect of changing the polarity, the dielectric relaxation, the viscosity, and other properties should be taken into account. As an example, the exothermicity parameter \( E \) varies with the solvent, and it was shown in I that it may be related to the gas-phase exothermicity \( E_0 \):

\[
E = E_0 - \frac{1}{4\pi} \int dr \left[ |D_0(r)|^2 - |D_1(r)|^2 \right].
\]

(2.19)

In an electrochemical experiment, for example, \( E_0 \) may be controlled by varying the cell voltage. In Fig. 5, we display the logarithm of the rate \( K \) [Eq. (1.2)] as a function of \((E - \delta_s)\) for propanol and hexanol. We assumed that \( g_0 \gg g_\perp \), so the effect of the back reaction is neglected, i.e., \( \tau_\perp = 0 \). The dashed line corresponds to a Debye model with \( \tau_\perp \) equal to \( \tau_0 \) of propanol. The multiple maxima in Fig. 5 result from the sharp maximum of the \( \tau(q) \) curve at \( q \neq 0 \) (see Fig. 4), whereas the function \( \sigma(\delta_s - E) \) has a maximum at \( q = 0 \). The Debye model does not have this characteristic for this particular value of \( V \), since its maximum is less sharp. Of course, by decreasing the value of \( V \), the two lower maxima should disappear, and the rate will eventually become nonadiabatic. This can clearly be seen in Fig. 6, where we plot the logarithm of the rate for propanol with various values of \( V \). As we decrease the value of \( V \) (given in the plots in cm\(^{-1}\)) the multiple maxima gradually disappear. This concludes our discussion of ET in solvents with a few relaxation times. In the next section, we shall analyze ET for solvents with a continuous distribution of time scales.

III. SOLVENTS WITH A CONTINUOUS DISTRIBUTION OF RELAXATION TIMES: THE COLE–DAVIDSON DIELECTRIC FUNCTION

Many polar solvents have a dielectric function that depends on \( \omega \) only through the dimensionless quantity \( \omega \tau_0 \), where \( \tau_0 \) is a characteristic solvent time scale, i.e., in Eq. (1.1) we have

\[
\chi = \chi(\omega \tau_0).
\]

(3.1)

The Cole–Cole, Cole–Davidson, and the Williams–Watts models are a few examples for dielectric functions of this form.\(^2\) These dielectric functions correspond to continuous distributions of relaxation times \( \tau \) [Eq. (2.1)], and \( \tau_0 \) is a parameter characterizing this distribution. It immediately follows from Eqs. (1.1), (1.5), (1.6), and (3.1) that \( M \) is only a function of \( y = t / \tau_0 \):

\[
M = M(t / \tau_0) = M(y).
\]

(3.2)

We thus have from Eqs. (1.4) and (3.2),

\[
g(t) = (\Delta \tau_0 / \delta_s)^2 f(t / \tau_0),
\]

(3.3)

and from Eq. (1.3) and (3.3),

\[
\sigma(\delta_s - E) = (\tau_0 / \delta_s) \text{Re} \left[ \int_0^\infty dy \exp[i(E - \delta_s)\tau_0 y / \delta_s] \right],
\]

(3.4a)

where

FIG. 5. The logarithm of the rate \( K \), in s\(^{-1}\), is plotted as a function of \((E - \delta_s) / \Delta\) for propanol (3), hexanol (6), and for a Debye model with \( \tau_0 \) equal to \( \tau_0 \) of the propanol (dashed curve). \( \varepsilon_\infty \) and \( \varepsilon_0 \) were taken to be the same as propanol. \( \Delta = 0.53\ \text{cm}^{-1},\ \nu = 5.3\ \text{cm}^{-1} \). The effect of the back reaction is neglected.

FIG. 6. The logarithm (base 10) of the ET rate (in s\(^{-1}\)) is plotted as a function of \((E - \delta_s) / \Delta\). The solvent parameters of propanol (Table 1) were used. The various curves correspond to different values of the nonadiabatic coupling \( V \), as indicated (in cm\(^{-1}\)) in the plot. The effect of the back reaction is neglected.
\[ f(y) = \int_0^y \int_0^y M(y_2) \, dy_2 \, dy_1. \]  

(3.4b)

The solvent time scale function assumes the form
\[ \tau(q) = \tau_0 F(q), \]  

(3.5a)

where \( F(q) \) does not depend on \( \tau_0 \) and is given by
\[ F(q) = \exp \left( -q^2 / 2 \right) \int_0^\infty dy \, \left\{ (1 - M^2(y))^{-1/2} \times \exp \left[ \frac{q^2 M(y)}{1 + M(y)} - 1 \right] \right\}. \]  

(3.5b)

We can now use Eqs. (3.5) and (1.13) to get the adiabaticity parameter
\[ \nu = (2\pi)^{1/2}(V^2/\hbar) \left[ F(q_a) + F(q_b) \right] \tau_0. \]  

(3.6)

In this section, we shall focus on the Cole–Davidson model, where
\[ \epsilon(\omega) = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty) / (1 - i\omega \tau_0)^\beta \]  

(3.7)

with \( 0 < \beta < 1 \). Note that the Debye model is a special case of the Cole–Davidson model, when \( \beta = 1 \) and \( \tau_0 = \tau_D \). Our analysis will be parallel to that of Sec. II. We start with the nonadiabatic limit, which requires the evaluation of the line shape function [Eq. (1.3)]. The extreme (short or long) time behaviors of \( g(t) \) can be analyzed in a straightforward way by using a Laplace transform, as explained in Sec. II and the Appendix. For short times we get
\[ g(t) = \frac{\Delta^2 t^2}{2k^2} \left[ 1 - a(t/\tau_0)^\beta + b(t/\tau_0)^{2\beta} + c(t/\tau_0)^{-1 + \beta} - d(t/\tau_0)^{3\beta} + \cdots \right], \]  

(3.8)

where
\[ a = \frac{2\epsilon_0/\epsilon_\infty}{\Gamma(3 + \beta)}, \]  

(3.9a)

\[ b = \frac{2(\epsilon_0/\epsilon_\infty - 1)(\epsilon_0/\epsilon_\infty)}{\Gamma(3 + 2\beta)}, \]  

(3.9b)

\[ c = \frac{2\epsilon_0/\epsilon_\infty}{\Gamma(4 + \beta)}, \]  

(3.9c)

\[ d = \frac{2(\epsilon_0/\epsilon_\infty)(\epsilon_0/\epsilon_\infty - 1)^2}{\Gamma(3 + 3\beta)}, \]  

(3.9d)

where \( \Gamma(x) \) is the gamma function. In general, \( g(t) \) will contain powers of the form \( t^n m^p \), where \( n \) and \( m \) are integers. Their order, thus, depends on the value of \( \beta \). For long times we have
\[ g(t) = (\gamma/\hbar) (t - t_0), \]  

(3.10)

where
\[ \gamma = \frac{1}{\hbar} \Delta^2 \beta(\epsilon_\infty/\epsilon_0) \tau_0, \]  

(3.11a)

and
\[ t_0 = \tau_0 \left[ \frac{\beta + 1}{2} - \beta(1 - \epsilon_\infty/\epsilon_0) \right]. \]  

(3.11b)

Note that for the Debye model \( t_0 = \tau_D \). We further have for the zeroth moment of \( M(t) \):
\[ \tau_M \equiv \int_0^\infty dt \, M(t) = \beta(\epsilon_\infty/\epsilon_0) \tau_0. \]  

(3.12)

We have calculated \( M(t) \) using Eqs. (A4), (A5), and (A8) together with a standard Laplace inversion numerical method.\(^{24}\) In Fig. 7, we show the logarithm of \( M(t) \) as a function of \( t/\tau_0 \) for \( \beta = 0.5 \) and several values of \( \epsilon_\infty/\epsilon_0 \). For the Debye model, this curve is a straight line. The nonlinear variation at short times is a signature of the infinite number of solvent time scales which exist in the Cole–Davidson model.

\( g(t) \) was calculated starting with the Laplace transform \( \hat{g}(s) \) [Eq. (A6)] and performing a standard Laplace inversion.\(^{24}\) The calculations were in agreement with the asymptotic analysis [Eqs. (3.10) and (3.11)]. The asymptotic (short or long time) limit of \( g(t) \), as given by Eq. (3.10), is the same as for the alcohol model or for the Cole–Davidson model. Consequently, we expect \( \sigma(x) \) to vary from a Gaussian [Eq. (2.14)] in the wings to a Lorentzian [Eq. (2.13), together with Eq. (3.11a)] in the line center. The dimensionless parameter, which controls the nature of \( \sigma(x) \), is
\[ \kappa^{-1} = \gamma/\Delta = \hbar^{-1} \sqrt{k_B T / \delta_a - \delta_b} \beta(\epsilon_\infty/\epsilon_0) \tau_0. \]  

(3.13)

For \( \kappa \gg 1 \) the line shape is Lorentzian [Eq. (2.13)] over many linewidths, and for \( \kappa \ll 1 \) it is a Gaussian [Eq. (2.14)]. In order to calculate the line shape function \( \sigma(x) \), we need to perform the Fourier transform [Eq. (1.3)]. Since the model has a continuous distribution of time scale, we found it difficult to obtain a good accuracy with a standard fast Fourier transform routine which uses a uniform spacing of points in \( y/t/\tau_0 \). Instead, we divided \( y \) into three regions. For \( y < 10^{-7} \), we used the short-time expansion [Eq. (3.8)]. For \( 10^{-7} < y < 5 \), we calculated \( f(y) \) at \( 10^4 \) points distributed exponentially according to
\[ y_n = 10^{-7} \exp(0.00173 n). \]  

(3.14)

In addition to this we added \( 10^4 \) linearly distributed points in this same interval \( (10^{-7}, 5) \). For \( y > 5 \), we used the asymptotic form [Eq. (3.10)]. We then calculated \( \sigma(x) \) using Eq. (3.4) by dividing the integral into three intervals. In the first

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$0 < y < 10^{-7}$ the integration was performed numerically, using an automatic adaptation NAG routine. In the second interval $10^{-7} < y < 5$ the integration was done numerically with a NAG routine appropriate for tabulated functions using the Gill–Miller finite differences method. In the third interval $y > 5$, the integration was done analytically. All calculations were done in double precision. The convergence was particularly slow for $\Delta \tau_0 / \hbar \approx 1$, and we had to include more points in the second integration interval. In Fig. 8(a), we present the line shape $\sigma(x)$ as a function of $x/\Delta$ for $\beta = 0.5$ and different values of $\varepsilon_m / \varepsilon_0$. As $\varepsilon_m / \varepsilon_0$ increases, the line shape becomes closer to the Gaussian limit. In Fig. 9, we display the line shape function $\sigma(x)$ for various values of $\beta$.

The analysis of $\sigma(x)$ corresponds, according to Eq. (1.14), to the nonadiabatic regime of the rate expression (1.2). To consider the crossover to the adiabatic regime, we need to analyze the adiabaticity parameter, Eq. (3.6). It can be rewritten, using Eqs. (1.9) and (1.8) and Eq. (3.6) as

$$\nu = \left[ 2\pi / (k_B T |\delta_a - \delta_b|) \right]^{1/2} (V^2 / \hbar) \times \left[ F(q_a) + F(q_b) \right] \tau_0.$$  

(3.15)

The function $F(q)$ was calculated numerically using Eq. (3.5). An accuracy up to the third digit was achieved for $F(q)$ ($0.4 < \beta < 1$ and $0.067 \varepsilon_m / \varepsilon_0 < 0.82$) by using a Gill–Miller algorithm, having tabulated the integrand of Eq. (3.5) at $\sim 10^4$ exponentially distributed points [see Eq. (3.14)] in the interval $[10^{-8}, 10]$. The contribution to the integration outside this interval is negligible. The values of $F(0)$ ($\varepsilon_m / \varepsilon_0$) are given in Table II for various values of $\beta$ and $(\varepsilon_m / \varepsilon_0)$. The behavior of $F(q)$ for $q > 2$ can be found analytically by using a short-time expansion of $M(t)$ and performing the integration [Eq. (3.5b)]. The short-time expansion of $M(t)$ may be obtained by taking the second derivative of $g(t)$ [Eq. (3.8)]. We thus get

$$F(q) = \frac{\Gamma(1/\beta - 1/2)}{2 \sqrt{2} \beta} \left[ 4 \Gamma(\beta + 1) \varepsilon_m / \varepsilon_0 \right]^{1/2} q^{1 - 1/\beta}.$$  

(3.16)

In Fig. 10(a), we show the solvent time scale function $\tau(q) / \tau(0)$ vs $q$ for various values of $\varepsilon_m / \varepsilon_0$ and for $\beta = 0.5$. In Fig. 10(b), we repeat this calculation for $\beta = 0.8$. For comparison we also included in Figs. 10(a) and 10(b) the solvent time scale function for the Debye model (dashed curve). Note that for the Debye model this curve is independent of $\varepsilon_m / \varepsilon_0$. Consequently, the $\beta = 0.8$ curves [Fig. 10(b)] are closer than the $\beta = 0.5$ curves [Fig. 10(a)], since the former are closer to the Debye limit. The asymptotic form [Eq. (3.16)] was found to hold within 0.1% for $q > 5$. As can be seen from Fig. 10, as $\beta$ decreases from the value 1 (Debye), the maximum of $F(q)/F(0)$ gets sharper but stays at $q \approx 1.6$. Using Eqs. (3.6) and (3.16), the adiabaticity parameter assumes the form

$$\nu = \begin{cases} 
\frac{2 \Gamma(1/\beta - 1/2) \tau_0}{\pi k_B T |\delta_a - \delta_b|} F(0), \\
\sqrt{\pi V^2 \Gamma(1/\beta - 1/2) \tau_0} \left[ \frac{4 \Gamma(\beta + 1) \varepsilon_m}{\varepsilon_0} \right]^{1/\beta} \\
\times [\delta_a - |E - \delta_a|^{1 - 2/\beta} + \delta_a - |E - \delta_a|^{1 - 2/\beta}]^{\Delta^{2/\beta - 2}}, 
\end{cases}$$  

(3.17)

The adiabaticity parameter depends on the electronic coupling $V$, the molecule–solvent interaction through a fractional power dependence on $|E - \delta_a|$ and $|E - \delta_b|$, the static properties of the solvent through a fractional power of $\varepsilon_m / \varepsilon_0$, the temperature, and the solvent polarity properties through $\Delta^{2/\beta - 2}$. This temperature dependence is absent in the Debye model.
where $\beta = 1$. In the adiabatic ($\nu \gg 1$) and static limit, the rate assumes the activated form [Eq. (1.17)], and the preexponential factor is given by

$$
A = \left[ \frac{1}{2F(0)} \tau_0 \cdot \frac{\sqrt{2B} [4k_B T|\delta_a - \delta_b|]^{1/2 - 1/B}}{\Gamma(1/\beta - 1/2) \{4\Gamma(\beta + 1)\varepsilon_m/\varepsilon_0\}^{1/\beta}} \times \left[ |E - \delta_a|^{1 - 2/\beta} + |E - \delta_b|^{1 - 2/\beta} \right]^{-1} \frac{1}{\tau_0},
$$
\[ (3.18) \]

This factor is inversely proportional to the solvent time scale parameter $\tau_0$. Since the maximum values for $F(0)$ are reached for $\beta = 1$ (see Table II), the adiabatic limit is more easily attained for the Debye solvent. The dynamical effects of the solvent given by the function $F(q)$ are stronger for non-Debye solvents because of the stronger dependence of $F(q)$ [and $\tau(q)$, Eq. (3.4)] on $q$. The dependence of the ET rate [Eq. (1.2)] on the solvent time scale parameter $\tau_0$ is displayed in Figs. 11–13. In these figures, we have assumed that $\tau(q_a) > \tau(q_b)$, and we have set $\tau(q_b) = 0$, neglecting the effect of the back reaction. The solid curves in Figs. 11 show the variation of the ET rate [Eq. (1.2)] with the solvent time scale parameter $\tau_0$ for $\beta = 0.5$ and $V = \Delta$. Small exothermicities are shown in Fig. 11(a), and larger exothermicities are shown in Fig. 11(b). For comparison we also display the nonadiabatic rates [Eq. (1.14)] (dashed curves). In Fig. 12, we repeat these calculations for $\beta = 0.8$. We note that the nonadiabatic rates always reach a plateau and become independent of $\tau_0$ for large $\tau_0$. This agrees with the static limit [Eq. (2.14)]. For larger values of $|E - \delta_a|$, before reaching the plateau, there is an extended region for which the nonadiabatic rate exhibits a fractional power dependence on $\tau_0$. This is clearly seen in the ($|E - \delta_a|/\Delta = 5$ curves in Figs. 11(b) and 12(b). For $\beta = 0.5$ we get $K \sim \tau_0^{-0.44}$, and for $\beta = 0.8$ we get $K \sim \tau_0^{-0.72}$ in this intermediate regime. Such fractional power dependence was recently observed by McGuire and McLendon. For smaller exothermicities, the intermediate regime shrinks, and the fractional power dependence is not observed. For large enough $\tau_0$, the nonadiabatic rate will eventually turn to the adiabatic limit. The point when this occurs depends on the adiabaticity parameter [Eq. (3.15)]. The actual rate will, therefore, decrease as $\tau_0^{-1}$ for large enough $\tau_0$ [Eq. (3.18)]. This behavior is clearly seen in Figs. 11 and 12, where the solid curves attain an asymptotic linear form with a slope of $-1$. In Fig. 13(a), we display the rate vs $\tau_0$ for $\beta = 0.5$, $|E - \delta_a|/\Delta = 0.01$, $\varepsilon_0/\varepsilon_m = 15.6$, and for several values of the coupling $V$. These curves are repeated for $|E - \delta_a|/\Delta = 5.2$ in Fig. 13(b). For $V/\Delta = 0.001$, the adiabaticity parameter becomes order 1 at very large values of $\tau_0$. The nonadiabatic rate with the plateau [Fig. 13(a)] or the fractional power

\[ q_a, q_b \ll 1 \]
\[ q_a, q_b \gg 1 \]

![FIG. 10. (a) The solvent time scale function $\tau(q)/\tau(0)$ is plotted for the Cole–Davidson model with $\beta = 0.5$. Curves A, B, C, and D correspond, respectively, to $\varepsilon_m/\varepsilon_0 = 0.82, 0.17, 0.096$, and 0.067. The dashed curve is for the Debye model. (b) The same as (a) for $\beta = 0.8$.](https://ojps.aip.org/jcpo/jcpcr.jsp)
dependence $\tau_0^{-0.44}$ [Fig. 13(b)] is clearly seen over a broad range of $\tau_0$ before the adiabatic limit sets in, and the limiting $\tau_0^{-1}$ form is attained. For large values of $V/\Delta$, the adiabatic limit sets earlier (for smaller values of $\tau_0$), and the intermediate (plateau or fractional power) regime is reduced. In Fig. 14, we display the logarithm of the rate vs $|E - \delta_2|/\Delta$ for $\beta = 0.5$, $\varepsilon_0/\varepsilon_m = 15.6$, $\tau_0\Delta/\hbar = 1$ for various values of the nonadiabatic coupling. As $V$ is increased, we see the appearance of multiple maxima. This effect was already discussed in the previous section (Figs. 5 and 6).

IV. DISCUSSION

In this article, we applied the theory developed in I to analyze ET processes in non-Debye polar solvents, whose dielectric function is characterized by multiple time scales. The effects of solvation are clearly separated into those arising from solvent polarity ($\varepsilon_0$ and $\varepsilon_m$) and dynamics [the frequency dependence of $\varepsilon(\omega)$] We have shown that the activation free energy depends only on the Pekar factor [Eq. (1.7)] and does not depend on the solvation dynamics. This result was derived previously by Marcus.5,6 for Debye solvents. The present theory shows that this result holds for non-Debye solvents as well. The solvation dynamics in the present theory is contained in $M(t)$, which is the normalized polarization correlation function of the solvent [Eq. (1.5)]. It may be calculated from a knowledge of the frequency-dependent dielectric function $\varepsilon(\omega)$ [Eq. (1.1)]. $M(t)$ enters our rate expression [Eq. (1.2)] through the line shape function $\sigma(x)$ [Eq. (1.3)] and the solvent time scale $\tau(q)$ [Eq. (1.11)]. Both quantities were analyzed in this article in detail for two typical models of $\varepsilon(\omega)$: one corresponding to solvents with a few dielectric relaxation time scales, such as alcohols, and the other to Cole–Davidson solvents, which
have a continuous distribution of time scales. \(^2\) Most commonly, the line shape function is extremely broad and assumes the static limit [Eq. (1.16)], whereby the solvent time scale is so slow compared with the linewidth that the line shape becomes independent of the solvent dynamics. Under these conditions, the rate assumes the activated form [Eq. (1.17)], and the solvent time scale enters only through the function \(\tau(q)\). It should be emphasized that the relevant solvent time scale depends not only on the solvent dynamics, but also on the reaction energetics \((q)\), [Eq. (1.12)]. The reason is that only specific solvent fluctuations around certain configurations (determined by \(q\)) affect the ET rate. A detailed analysis of \(\tau(q)\) was made. \(\tau(q)\) is displayed in Fig. 4 for linear alcohols and in Fig. 10 for Cole–Davidson solvents. The dependence on \(q\) is relatively weak (power low). For the alcohols it behaves as \(q^{-1}\) for large \(q\), whereas for Cole–Davidson solvents it behaves as \(-q^{-1/2}\). \(\tau(q)\) also determines the reaction adiabaticity via the adiabaticity parameter \(\nu\) [Eq. (1.13)], which controls the crossover from the nonadiabatic to the adiabatic regime. As the solvent time scale becomes slow, a nonadiabatic reaction will become adiabatic. For the Cole–Davidson model, we find that the rate scales as \(\tau_0^{-1}\) for large \(\tau_0\), where the adiabatic limit holds. For smaller values of \(\tau_0\), and provided \(V\) is sufficiently small and \(|E - \delta_e|/\Delta\) sufficiently large, we find a time scale range for which the rate varies as \(-\tau_0^{-\beta}\). This range can extend over several orders of magnitude. This is in qualitative agreement with the fractional power dependence on \(\tau_0\) observed by McGuire and McLeond\(^{25}\) in glycerol.

A major advantage of the present formulation is that it can be easily extended in various ways. First, in general a polar solvent is characterized by a frequency and wave vector dependent dielectric function \(\epsilon(k,\omega)\). In the present analysis, we used only the long wavelength \((k = 0)\) limit of \(\epsilon(k,\omega)\). Even a Debye solvent should have a multitude of time scales, once the spatial dispersion is included.\(^{26}\) The theory developed in I contains \(\epsilon(k,\omega)\) and thus allows us to incorporate it. In addition, the incorporation of other degrees of freedom, such as internal molecular vibrations,\(^{27}\) can be made easily, using the same models developed for nonlinear optical line shapes,\(^{3,9}\) and it will only affect \(M(t)\).

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APPENDIX: ASYMPTOTIC ANALYSIS OF THE TIME EVOLUTION

The limiting (short- or long-time) behaviors of the various quantities appearing in this article may be obtained as follows: we first introduce the Laplace transform of \(\chi(t)\). We define

\[ \mathcal{L}\{\chi(t)\} = \int_0^\infty e^{-st} \chi(t) \, dt \]
\[ \chi(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} d\omega \chi(\omega) \exp(-i\omega t) \quad (A1) \]

and the Laplace transform of \( \chi(t) \):
\[ \tilde{\chi}(s) = \int_{0}^{\infty} dt \chi(t) \exp(-st) \quad (A2) \]

and
\[ e(s) = \varepsilon_0 + (\varepsilon_0 - \varepsilon_\infty) \tilde{\chi}(s) \quad (A3) \]

The Laplace transform of any function of time \([g(t), M(t), \text{etc.}]\) will be defined in an analogous manner to Eq. (A2) and will be denoted \( \tilde{g}(s) \), \( \tilde{M}(t) \), etc. Making use of Eqs. (A1)–(A3) and Eqs. (1.4)–(1.7), we have
\[ \tilde{Q}(s) = (1/e(s) - 1/\varepsilon_0)s^{-1} \quad (A4) \]
\[ \tilde{M}(s) = (1/\varepsilon_\infty - 1/\varepsilon_0)^{-1}\tilde{Q}(s) \quad (A5) \]

and
\[ \tilde{g}(s) = \frac{\Delta^2\tilde{M}(s)}{s^2} \quad (A6) \]

For solvents with \( N \) relaxation times, we have
\[ e(s) = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty) \sum_{j=1}^{N} \frac{\gamma_j}{1 + s\tau_j} \quad (A7) \]

For the Cole–Davidson model, we have
\[ e(s) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{(1 + s\tau_0)^\alpha} \quad (A8) \]

The short-time behavior of a function \( f(t) \) may be obtained from \( \tilde{f}(s) \) by expanding it in powers of \( 1/s \) and using the relation
\[ f(t) = At^\alpha \quad (A9a) \]
\[ \tilde{f}(s) = A\frac{\Gamma(1+\alpha)}{s^{1+\alpha}} \quad (A9b) \]

where \( \Gamma \) is the gamma function. In particular for \( \alpha = 0 \):
\[ f(0) = \lim_{s \to \infty} s \tilde{f}(s) \quad (A10) \]

The long-time behavior may be obtained by expanding \( \tilde{f}(s) \) in powers of \( s \) for \( s \to 0 \). If this series diverges as
\[ \tilde{f}(s) = \frac{A}{s^2} + \frac{B}{s} + \cdots \quad (A11a) \]

then
\[ f(t) = At + B + \cdots \quad (A11b) \]

Finally, if \( \tilde{f}(s) \) is analytical at \( s = 0 \), we have the relation
\[ \tilde{f}(s) = \sum_{n=0}^{\infty} \frac{a_n}{n!} s^n \quad (A12a) \]

These relations will be used in our asymptotic analysis presented in Secs. II and III.

6. S. I. Pekar, Zh. Eksp. Teor. Fiz. 19, 796 (1949): Eq. (1.7) may be derived from Eq. (1.6) by considering the Laplace transform of \( Q(t) \). \( \tilde{Q}(s) \) [Eq. (A4)] and making use of Eq. (A10).