

SOLVATION DYNAMICS STUDIED BY PICOSECOND FLUORESCENCE: MICROSCOPIC REORIENTATION AND LONGITUDINAL RELAXATION OF THE SOLVENT

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The dynamics of the Time-Dependent Fluorescence Shift (TDFS) of a rigid polar excited probe dissolved in alcohol solvents at different temperatures have been studied by picosecond time-resolved spectroscopy. The results are compared to previously published results on well characterized polar systems. These results show that solvation dynamics in such systems are strongly scaled by the microscopic (single-particle) reorientation time τ_M of the solvent molecules and/or by the (macroscopic) longitudinal relaxation time τ_L of the solvent. The key point governing this scaling is the relative interaction between the solvent molecules and the probe compared to the interaction between the solvent molecules. It is also shown that specific interactions, such as hydrogen bonded-complex formation, may play an important role.

KEY WORDS: Solvation dynamics, picosecond TDFS, dielectric phenomena.

I. INTRODUCTION

Ware *et al.*, have shown¹ that time-resolved spectroscopy on a nanosecond time scale is a powerful tool for studying the solvation dynamics of an excited polar probe dissolved in polar solvents because during the solvation process the emission spectrum of the probe shifts to higher wavelengths. Studying the time dependence of this shift, one obtains information about the dynamics of the solvent cage reorganization. Previously the first experimental results obtained in our laboratory on the picosecond Time-Dependent-Fluorescence-Shift (TDFS) of an optically excited probe molecule dissolved in alcohol solvents at room temperature were presented.²

This work was followed by several papers^{3–13} concerning the solvation dynamics, on a picosecond and subpicosecond time scale, of various probes dissolved in various different polar solvents. From these studies it was shown^{7–13} that the observed *solvation dynamics is not simply related to the relaxation time of the solvent*, as calculated from the known frequency dependence of the (macroscopic) orientation

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reaction field of the solvent using continuum models.^{14–16} These theoretical models predict characteristic solvation times of the order of the longitudinal relaxation time τ_L of the solvent defined as^{14–17}:

$$\tau_L = (\epsilon_\infty/\epsilon_0)\tau_D \quad (1)$$

where ϵ_∞ and ϵ_0 are the dielectric constant of the solvent in an electric field of infinite frequency (ϵ_∞) and in a static field (ϵ_0), and τ_D is the Debye time or the bulk dielectric relaxation time of the solvent. On the contrary, the experimentally observed solvation dynamics often exhibit a slow component with a characteristic time much longer than τ_L and ranging between τ_L and τ_D ($\tau_L \ll \tau_D$ in highly polar solvents for which $\epsilon_0 \gg \epsilon_\infty$, see Eq. (1)). Considering that τ_L and τ_D are, by definition, macroscopic quantities, the absence of a simple correlation between the observed characteristic solvation times and τ_L (τ_D) showed that the macroscopic approach, where the solvent is considered as a dielectric continuum, is not a realistic framework. In other words, a microscopic approach which takes into account the molecular aspect of the solvation process is necessary. New theoretical models were then developed showing^{18–21} that the values of the characteristic solvation times should range between τ_L and τ_D , in qualitative agreement with experimental results. Nevertheless, *quantitative agreement has not yet been obtained* showing that there is still room for refinement of the model.

The experimental studies of the TDFS are generally made in highly polar solute-solvent systems in order to obtain fluorescent spectral shifts as large as possible, which allows for greater precision. As a consequence, highly polar solvents are used. Also probe molecules often exhibit a large charge redistribution (Internal Charge Transfer: ICT) in the excited state leading to: (a) an excited charge distribution closer to an extended dipole than the point dipole generally assumed in theoretical models, and (b) a high dipole moment μ^* (≥ 10 D,^{8,13} for example.) when the excited state is a $\pi^*-\pi$ state.

Three important points have to be noted regarding the conditions near such an excited probe:

- 1) The sudden electric field induced by the electronic excitation of the probe is highly inhomogeneous on the solvent molecular scale;
- 2) The dipolar interaction δE between the solute molecule and a solvent molecule may be larger than kT leading to local dielectric saturation of the solvent, as recently shown²² in the case of a point charge;
- 3) δE may be also larger than δe , the solvent-solvent molecular interaction.

Because these considerations did not receive sufficient attention in any of the solvation dynamics studies, two sets of experimental results will now be discussed. These sets of experimental results are taken from our recent work on TDFS¹³ in highly polar aprotic solvents and from the work of Fleming *et al.*⁷ on LDS-750 probe.

In previous work¹³ a rigid polar probe molecule, 3-methyl-2,3,6,7,8-pentahydroquinolizino-4h-(1,9-g,h)-1-benzoxazine-1,4-2-one, (MPQB) (Figure 1) was selected in order to avoid possible intramolecular rearrangements which may induce a fluorescent spectral shift as a function of time.⁹ Such a rearrangement would lead to

excited solute ($\delta E > kT$ and/or $\delta E > \delta e$) cannot be described in the framework of a continuum model, in which the assumption $\delta E \ll kT$ is always implicitly made. The solvent molecules lose their dipolar (long-range) orientational correlations and relax in an individual manner (free from mutual dipolar interactions) leading to the correlation between τ_R and τ_M as observed from the TDFS behaviour of MPQB;¹³

- 2) For the outer-shell solvent molecules, the interaction with the probe is weaker than the interaction with the solvent molecules of the first shell. Therefore, their dipolar (long-range) orientational correlations are maintained and these molecules relax in a collective way (as a bulk dielectric continuum) on a shorter time scale which should be τ_L . Unfortunately, in the experimentally accessible temperature range for the solvents used (DMF, PC), τ_L is very short (≤ 20 ps) and well under our experimental time resolution (≈ 40 ps). In such a situation, the part of the TDFS related to this process appears as an instantaneous shift on our time scale,¹³ and the presence of a relaxation time correlated to τ_L in the TDFS dynamics was difficult to observe unambiguously from this work.¹³

Subpicosecond results on solvation dynamics of a weakly polar excited probe (LDS-750) dissolved in different polar solvents were recently reported.⁷ In light of the above discussion, it is interesting to discuss briefly these results. Indeed this probe molecule (LDS-750) has the particularity to be less polar in its first excited singlet state than in its ground state, contrary to currently used probe molecules, like MPQB for example, for which: $\mu^* > \mu^0$, where $\mu^*(\mu^0)$ is the permanent dipole moment of the probe in its excited (ground) state. As a consequence, in the case of LDS-750, for which $\mu^* < \mu^0$, the dipolar interaction between the excited probe and its polar environment is very weak, as shown in.⁷ On the other hand, it appears from the experimental curves and data reported in⁷ that there is a good quantitative agreement between the experimental single exponential characteristic time (τ_R) of the TDFS of the probe (LDS-750) and the longitudinal relaxation time τ_L of the solvent, when τ_L is defined in Eq. (1) with $\epsilon_\infty = n^2$ (see the end of Note 1 and the Appendix) as noted by the authors themselves. This observed correlation supports the hypothesis given here regarding the relaxation time scale of the outer-shell solvent molecules in weak interaction with the probe, such as in the picosecond study¹³ of the TDFS of MPQB dissolved in non-aggregated polar solvents. Indeed, the electronic excitation of LDS-750 induces an increased delocalization of the net charges along its molecular skeleton;⁷ under these conditions, after excitation of the probe (LDS-750) all the polar solvent molecules (some of which may be strongly interacting with the solute in its more polar ground state, including specific interactions such as complex formation⁷) can have only weak interactions with the probe molecules. As a consequence, they instantaneously recover their orientational correlations and they relax in a collective way (as a bulk dielectric continuum) on the time scale of τ_L according to the continuum model prediction.

These two sets of new experimental results^{7,13} strongly support the hypothesis of the existence of a *hierarchy of standard relaxation mechanisms* in polar solute-solvent systems:

- 1) A fast process (with $\tau_R = \tau_L$) related to the collective reorientation of the solvent molecules weakly interacting with the solute;
- 2) A slower process (with $\tau_R = \tau_M > \tau_L$, see Eq. (1) and Eq. (2) with $\epsilon_0 > \epsilon_\infty$) related to the individual reorientation of the solvent molecules strongly interacting with the solute.

The existence of this last process is consistent with the observation of a slow component (compared to τ_L) in solvation dynamics of many polar systems.^{7,13}

In these polar systems^{7,13} studies have been performed on chemical systems which do not possess specific interactions such as hydrogen bonded-complex formation between excited probe and solvent molecules. But in the case of highly polar excited probes such as MPQB dissolved in alcohols, solute-solvent H-bond formation in the excited state may strongly affect the TDFS of the probe leading to the general conclusion that, in a first step, such solute-solvent systems are not ideal probes for solvation dynamics studies.⁹ It's now worthwhile to turn to studies of the relaxation mechanisms in highly interacting systems, such as alcohol solvents for which a lot of physical data are available.^{27,29-43} This is the aim of this paper. In order to do this, a careful analysis of the picosecond time evolution of the whole emission spectrum of MPQB dissolved in various alcohols at different temperatures has been performed. In the next section the experimental set-up is briefly described. In the third section the effect of varying the temperature on the respective contributions of the specific solute-solvent interaction, due to hydrogen bonded-complex formation in the excited state, and of the non-specific solvation process to the TDFS of MPQB is demonstrated. The fourth section discusses to what extent the picosecond observable part of the TDFS can be correlated with the longitudinal relaxation time τ_L of the solvent. The conclusion deals with to what extent the solvation dynamics of polar solute-solvent systems is scaled by the solvent time (s) τ_M and/or τ_L , depending on the nature and the relative intensity of the different interactions existing in the medium.

II. EXPERIMENTAL

As in the previous study,¹³ the rigid polar probe MPQB (Figure 1) was selected in order to avoid intramolecular rearrangements. This probe exhibits a strong charge redistribution (ICT) in its first excited singlet state, S_1 , from the electron donor group (the molecular moiety including the tertiary amino group) to the electron acceptor group (the molecular moiety associated with the ring containing the carbonyl group). This ICT induces important charge changes on specific atoms upon electronic excitation. That is shown in Figure 1, where the significant net atomic charges were calculated by the semi-empirical PPP-SCF-CI quantum chemical (π -electron density) and Del Re's (σ -electron density) methods. The drastic change of the charge densities on the main proton acceptor sites (the O atom of the carbonyl group and the N atom of the same ring) can induce solute-solvent hydrogen bonded-complex formation in the excited state (S_1) with proton donor solvents such as alcohols.

The time evolution of the whole emission spectrum of MPQB dissolved in various alcohols at different temperatures has been performed using a picosecond

spectrometer described in detail elsewhere.⁴⁴ The solvents were used without further purification as received from Aldrich Chemical. Typical concentrations lie in the range: $5 \times 10^{-4} - 10^{-3}$ M; there were no concentration effects. In all the experiments reported here, the lifetime of the excited state S_1 of MPQB was longer than 1 ns so that relaxation processes with characteristic times (τ_R) in the range 40 ps (our experimental time resolution)—1 ns can be studied in good conditions. The temperature was kept constant within $\pm 1^\circ\text{C}$ using a Specac cryostat P/N 21000.

III. EXPERIMENTAL RESULTS

Figure 2 displays the time evolution of the whole emission spectrum of MPQB

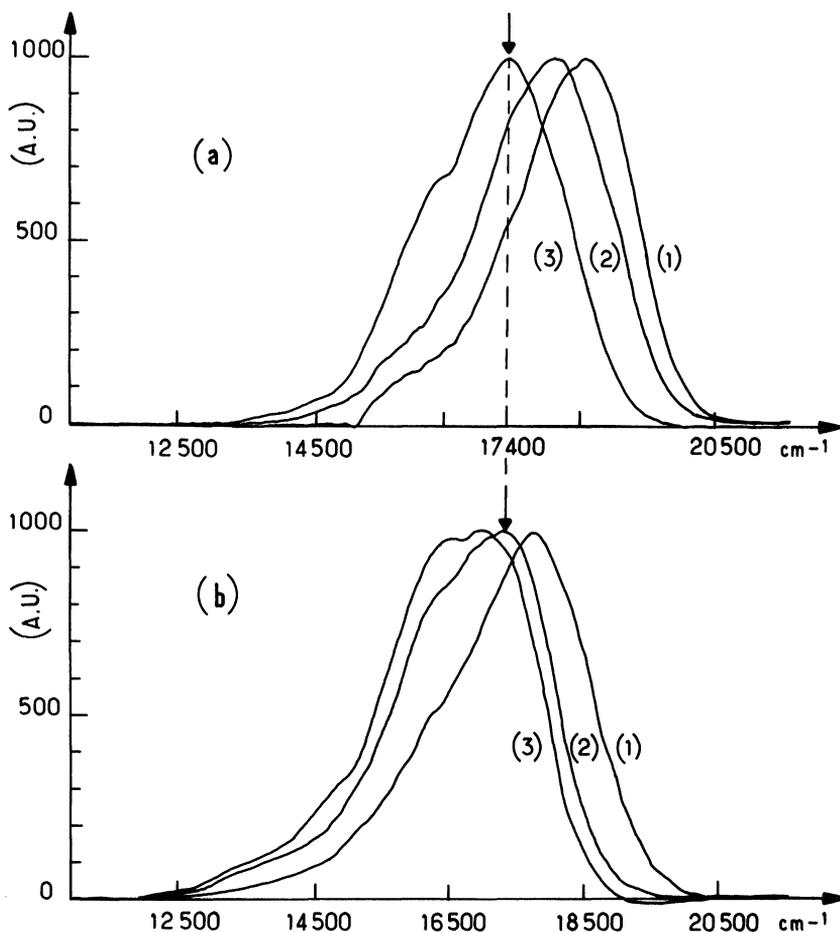


Figure 2 Time evolution of the emission spectrum of the MPQB probe in *n*-Propanol at two temperatures:

(a) $T = -25^\circ\text{C}$;

(1) $t = 50$ ps; (2) $t = 150$ ps; (3) $t = 450$ ps

(b) $T = 18^\circ\text{C}$ (room temperature);

(1) $t = 100$ ps; (2) $t = 200$ ps; (3) $t = 400$ ps.

dissolved in *n*-Propanol after optical excitation at 0.355 μm (time $t = 0$), at two temperatures: -25°C (Figure 2a) and room temperature (18°C) (Figure 2b).

III-1. Low Temperature

At low temperature (Figure 2a), this time evolution can be described as follows.

- 1) In a first step, one observes the red shift of a main fluorescence band, without noticeable changes in its shape. At later times, the wavenumber of the maximum of this band is stabilized, at around: $\tilde{\nu}_\infty \approx 17400 \text{ cm}^{-1}$. This behaviour is quite comparable to the time evolution of the emission spectrum of MPQB in polar aprotic solvents¹³ (with the same f.w.h.m. of about 2000 cm^{-1});
- 2) In a subsequent step, a new fluorescence band appears around $16,500 \text{ cm}^{-1}$ and then grows in.

Because such a red shifted band ($16,500 \text{ cm}^{-1}$) is never observed in polar aprotic solvents,¹³ these two effects can be unambiguously attributed to:

- 1) The overall solvent cage relaxation around free (uncomplexed) excited probe molecules leading to the continuous red shift of the main band towards $17,400 \text{ cm}^{-1}$;
- 2) The formation of H-bonds between the solvent and specific sites of the excited solute molecular skeleton giving rise to a new species (hydrogen bonded-complex) emitting around $16,500 \text{ cm}^{-1}$, this extra red shift ($\approx 1000 \text{ cm}^{-1}$) being due, in part, to the greater stabilization of the S_1 state of the probe under specific H-bond formation.^{24,45} The dynamics of this last process (complex formation) seems to be slower than the first one (the overall solvent cage relaxation).

III-2. Room Temperature

At room temperature (Figure 2b), the two effects mentioned above are not clearly separated on the picosecond time scale: The whole emission spectrum evolves in such a way that its long time evolution is strongly perturbed by the increase of the complex band at $16,500 \text{ cm}^{-1}$. The same situation is observed in *n*-Butanol. A different situation is present in long chain alcohols (Pentanol, for example) and also in short chain and/or strong proton donor alcohols (Methanol, Ethanol, Ethylene-Glycol, 3F-Ethanol, for example²⁴).

In long chain alcohols, such as Pentanol, for example (see Figure 2 of Ref.⁶) the complex band ($16,500 \text{ cm}^{-1}$) appears slowly and remains sufficiently weak so that the TDFS dynamics appear as a progressive red shift of a whole band without noticeable shape change. Under such conditions, the observed TDFS is essentially due to the overall solvent cage relaxation as in the case of *n*-Propanol at -25°C .

On the other hand, for short chain and/or more acidic alcohols, the situation is more complicated. The red shifted band due to the complex appears in a time which is less than the resolution time of our instrument. Under such conditions, the

observed TDFS is the result of the two competing processes, the formation of the complex and the overall solvent cage relaxation. These two effects are very difficult to separate and information about solvent relaxation dynamics is impossible to obtain.

However, we found that for linear aliphatic alcohols ranging from Methanol to Pentanol, it's possible to separate the respective effects of complex formation and of the "pure" solvent relaxation process on the TDFS of MPQB on the picosecond time scale by working at sufficiently low temperature in such a way that the dynamics of complex formation and of the "pure" solvent relaxation process appear on different time scales and become distinct within the limits of our experimental time resolution.

IV. DISCUSSION

IV-1. Analysis of the "Pure" Solvent Relaxation Process

In order to characterize the overall solvent cage relaxation, the wavenumber of the emission maximum is plotted against time ($\tilde{\nu}_{EM}(t)$) for the first step of the observed TDFS, as illustrated above in the case of *n*-Propanol at -25°C . Three such typical curves are shown in Figure 3. Taking into account the pulse duration of the laser

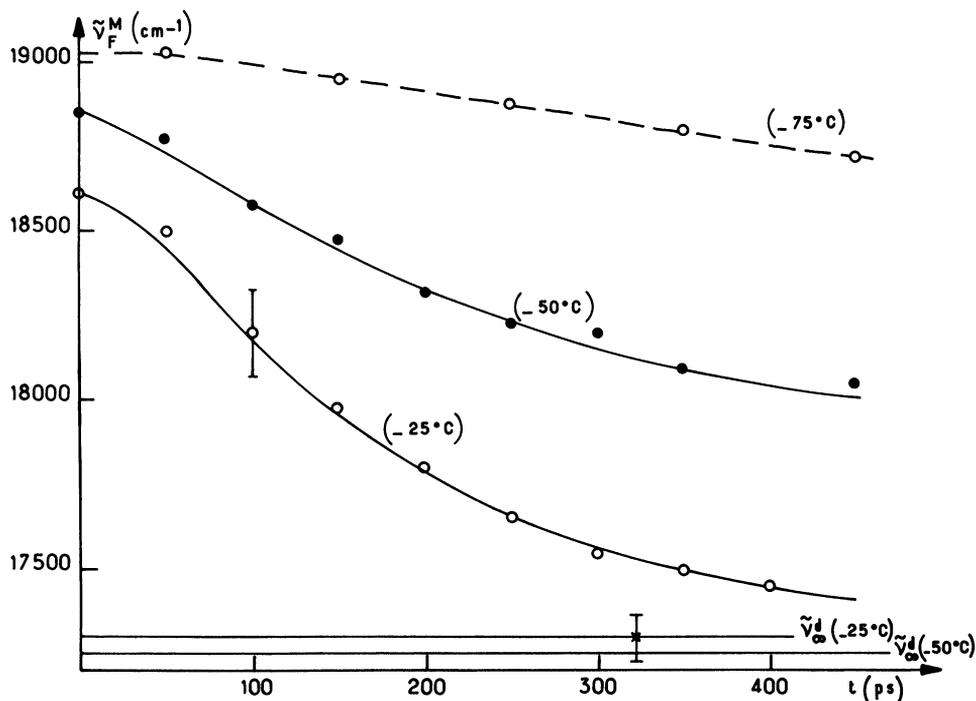


Figure 3 Time evolution of the wavenumber of the maximum $\tilde{\nu}_{EM}(t)$ of the main band of the emission spectrum of MPQB in *n*-Propanol at different temperatures. The vertical bars indicate typical experiment uncertainty in the determination of $\tilde{\nu}_{EM}(t)$ and $\tilde{\nu}_\infty$. The continuous lines are the fits obtained from the procedure described in the text.

excitation source (f.w.h.m. $\sigma = 40$ ps), we were able to simulate by a single exponential function of characteristic decay time, τ_R , the quantity:

$$\delta\tilde{\nu}_{EM}(t) = \nu_{EM}(t) - \tilde{\nu}_\infty = \delta\tilde{\nu}_{EM} \cdot \exp(-t/\tau_R) \quad (3)$$

where $\tilde{\nu}_\infty$ is the maximum wavenumber when the emission spectrum is stabilized, and $\delta\tilde{\nu}_{EM}$ is the amplitude of the TDFS.

All of the measured ($\tilde{\nu}_\infty$) and calculated ($\delta\tilde{\nu}_{EM}$, τ_R) values according to this procedure are given in *Table 1*. Also reported in *Table 1* are the dielectric parameters $\{\epsilon_0, \epsilon_\infty = n^2, g_K, \tau_D\}$ of the studied alcohols and the longitudinal relaxation time, τ_L , as calculated from Eq. (1) and the microscopic (single-particle) reorientation time, τ_M , as calculated from Eq. (2). The high value of g_K , Kirkwood's correlation factor, is due to H-bond aggregation of alcohols.²⁷

The strong correlation between τ_R and τ_L leads to the conclusion that these solvents collectively relax around the excited MPQB probe, on the time scale of τ_L , according to the continuum model prediction. Indeed, this conclusion is consistent with the arguments recalled in the introduction and developed in previous work¹³. The molecular dipole-dipole interaction δE between an excited probe molecule such as MPQB ($\mu^* > 15$ D,¹³) and one of its nearest-neighbor solvent molecules (with a permanent dipole moment μ) may be roughly estimated from the quantity: $\mu^*\mu/\epsilon_\infty R^3$, where $\epsilon_\infty = n^2$ (≈ 2.0 in the studied polar liquids) describes the electronic polarization of the solvent and R is the effective distance between the excited solute's extended dipole of finite length (≈ 6 Å in the case of MPQB) and a molecular solvent dipole in the first solvent shell. In the case of alcohols, ($\mu \approx 1.6$ D), δE falls in the range of kT and is small compared to the alcohol-alcohol interaction δe , which is essentially due to H-bond aggregation ($\delta e \approx E_{HB} \geq 5.0$ kcal/M^{29,30}). This situation induces strong orientational correlations, as reflected by the high value of g_K (see *Table 1*), as mentioned above. Under these conditions, even with a highly polar excited probe such as MPQB ($\mu^* > 15$ D), the solute-solvent interaction due to electronic excitation of the probe is not sufficient to break orientational correlations between alcohol solvent molecules, which then relax in a collective way as a bulk dielectric continuum on the time scale of τ_L .

These new experimental results on the solvation dynamics of MPQB in alcohols can be compared to the experimental results obtained with the probe LDS-750.⁷ Figure 4 illustrates the strong correlation between the characteristic time (τ_R) of the TDFS of these two molecular systems (MPQB in alcohols and LDS-750 in various polar protic and aprotic solvents) and the longitudinal relaxation time (τ_L) of the solvent. These results strongly support the hypothesis given here on the collective reorientation (scaled by τ_L) of polar solvent molecules around an excited polar probe when the excited solute-solvent interaction is too weak to disrupt orientational correlations between relaxing solvent molecules.

IV-2. Analysis of Hydrogen Bonded-Complex Formation

In addition to studying the "pure" solvent relaxation process at various temperatures for given alcohols as shown above, one can study the hydrogen bonded-complex

Table 1 $\{\epsilon_0, \epsilon_\infty = n^2, g_K, \tau_D\}$: Solvent parameters calculated by interpolating the reported values from the cited References (the optical refraction index was calculated from the reported value $n_D^{20,42}$ and from the molar refraction law: $R = [(n^2 - 1)/(n^2 + 2)](M/d) = cst^{42}$, where M is the molecular weight and d is the density of solvent; the density, d , of the studied alcohols at different temperatures was obtained from Ref. 27).

τ_M : microscopic reorientation time of the solvent molecules calculated from Eq. (2);

τ_L : longitudinal relaxation time of the solvent calculated from Eq. (1);

$\{\tau_R, \sigma_{EM}, \tilde{\nu}_\infty\}$: characteristic parameters of the TDFS of MPQB in alcohols.

References: (a) ^{35,36,37}; (b) ^{35,36,38,39}; (c) ^{31,37,40,41}; (d) ^{31,41}

| Solvent (temperature) | ϵ_0 | $\epsilon_\infty = n^2$ | g_K | $\tau_D(ps)$ | $\tau_M(ps)$ | $\tau_L(ps)$ | $\tau_R(ps)$ | $\delta\nu_{EM}(cm^{-1})$ | $\tilde{\nu}_\infty(cm^{-1})$ | Ref. |
|--------------------------------------|--------------|-------------------------|-------|--------------|--------------|--------------|--------------|---------------------------|-------------------------------|------|
| Methanol ($-90^\circ C$) | 70.3 | 1.90 | 3.37 | 2,390 | 479 | 64 | 69 \pm 25 | 600 \pm 200 | 17,250 \pm 75 | (a) |
| Ethanol ($-30^\circ C$) | 33.5 | 1.92 | 3.23 | 1,110 | 236 | 64 | 55 \pm 20 | 1,250 \pm 150 | 17,300 \pm 75 | (b) |
| Ethanol ($-50^\circ C$) | 38.5 | 1.94 | 3.32 | 2,280 | 469 | 115 | 123 \pm 25 | 950 \pm 150 | 17,300 \pm 50 | (b) |
| Ethanol ($-70^\circ C$) | 44.4 | 1.97 | 3.35 | 6,350 | 1,280 | 282 | 280 \pm 40 | 1,050 \pm 100 | 17,275 \pm 50 | (b) |
| Ethanol ($-80^\circ C$) | 47.0 | 1.98 | 3.38 | 11,300 | 2,296 | 476 | 473 \pm 50 | 1,400 \pm 150 | 17,250 \pm 75 | (b) |
| Ethanol ($-90^\circ C$) | 51.0 | 1.99 | 3.41 | 18,600 | 3,707 | 726 | 783 \pm 75 | 1,400 \pm 150 | 17,250 \pm 75 | (b) |
| <i>n</i> -Propanol ($-25^\circ C$) | 28.0 | 1.97 | 3.50 | 2,200 | 434 | 155 | 175 \pm 25 | 1,500 \pm 100 | 17,350 \pm 50 | (c) |
| <i>n</i> -Propanol ($-50^\circ C$) | 33.5 | 2.00 | 3.64 | 9,240 | 1,743 | 552 | 580 \pm 60 | 1,500 \pm 150 | 17,250 \pm 50 | (c) |
| Pentanol ($18^\circ C$) | 15.3 | 1.98 | 3.39 | 1,080 | 226 | 140 | 144 \pm 30 | 1,300 \pm 100 | 17,500 \pm 50 | (d) |

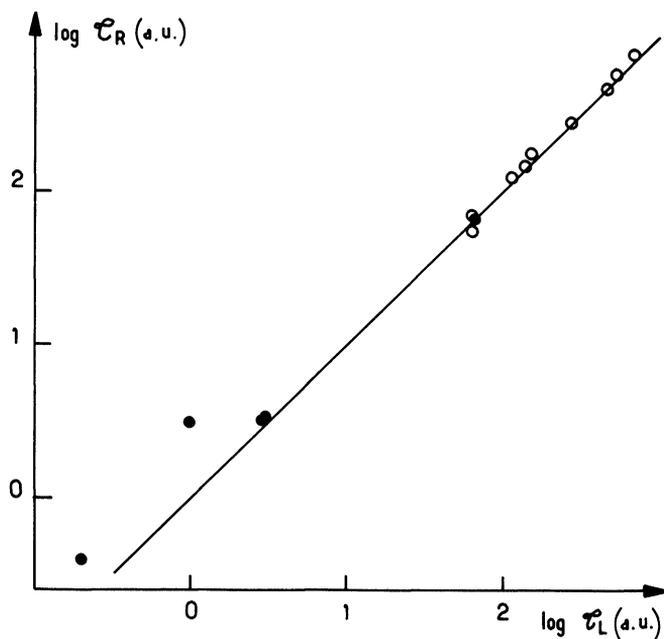


Figure 4 Illustration of the correlation between the TDFS characteristic time, τ_R , for two different probes and the corresponding longitudinal relaxation time, τ_L , of the solvents:

(○) MPQB in different alcohols, (see *Table 1*).

(●) LDS-750 in different polar solvents, as reported in Ref. 7 (one notes that the two lower points slightly out of the correlation line correspond to: $\tau_L \leq 1$ ps, with an experimental time resolution ≈ 0.5 – 1.0 ps²).

formation process as revealed by the time evolution of the whole emission spectrum of MPQB dissolved in alcohols, as illustrated by the case of *n*-Propanol at 18°C.

The red shifted band (around $16,500 \text{ cm}^{-1}$) has already been attributed to excited solute-solvent hydrogen bonded-complex formation. In small and/or strong proton donor alcohols at room temperature, the emission spectra of complexed and uncomplexed probe molecules strongly overlap in such a way that the spectral evolution of the whole emission spectrum of MPQB during complex formation is seen as a progressive red shift towards about $16,500 \text{ cm}^{-1}$ on a picosecond time scale: The emission band of complexed probe molecules (around $16,500 \text{ cm}^{-1}$) increases at the same time that the emission band of uncomplexed probe molecules decreases and reaches its stationary position (around $17,400 \text{ cm}^{-1}$).

This apparent shift may be simulated by a single exponential law using the procedure described above. Following this procedure, a characteristic time, τ_1 , was determined, which may be associated with the hydrogen bonded-complex formation dynamics. Values of τ_1 are reported in *Table 2* as well as the solvent characteristic times, τ_L and τ_M . We can note the correlation between the determined characteristic time, τ_1 , and the microscopic reorientation time, τ_M , of the alcohol molecules.

Table 2 Characteristic times of the TDFS of Coumarin 153 (Cu153): (τ_1 , τ_2 , τ_3) (Ref.⁸), and of MPQB, (τ_1). The solvent times, τ_M and τ_L , are calculated as in *Table 1* from the cited References (except for Cu153 where τ_M was estimated as: $2\tau_D/9$, according to Eq. (2) with $\epsilon_0 \gg n^2$ and $g_K \approx 3$ in alcohols, and from τ_D values as reported in Ref.⁸). The results for Cu153 in N-Methylpropionamide (which is a strongly aggregated solvent⁴³ able to form H-bonded complexes as alcohols) are not given here because Ref.⁴³ contains an error in the dielectric relaxation times of this solvent. Namely, in *Table 3* of Ref.⁴³ the reported dielectric relaxation times are erroneous for N-Methylacetamide and N-Methylpropionamide: They have to be multiplied by 10 in order to be consistent with the dielectric data reported in Figure 1, Figure 5 and *Table 4* of this same work⁴³

| Solute/solvent (temperature) | τ_1 (ps) | τ_M (ps) | τ_2 (ps) | τ_L (ps) | τ_3 (ps) | Ref. |
|-----------------------------------|---------------|---------------|---------------|---------------|---------------|------|
| Cu153/Ethanol (253 K) | 150 | 143 | 31.4 | 37.7 | — | [8] |
| Cu153/ <i>n</i> -Propanol (295 K) | 78.8 | 97.3 | 9.3 | 39.4 | — | [8] |
| Cu153/ <i>n</i> -Propanol (273 K) | 245 | 208 | 87.6 | 74.5 | — | [8] |
| Cu153/ <i>n</i> -Propanol (251 K) | 430 | 467 | 101 | 151 | — | [8] |
| Cu153/ <i>n</i> -Propanol (232 K) | 1,110 | 1,102 | 254 | 314 | 29 | [8] |
| Cu153/ <i>n</i> -Propanol (221 K) | 2,560 | 2,140 | 572 | 570 | 86 | [8] |
| Cu153/ <i>n</i> -Butanol (253 K) | 747 | 716 | 189 | 272 | 45 | [8] |
| Cu153/2-Propanol (253 K) | 648 | 678 | 103 | 231 | — | [8] |
| MPQB/Ethylene-Glycol (T_A) | 52 | 51 | — | 9.2 | — | [34] |
| MPQB/Methanol (T_A) | (<40) | 14 | — | 3.4 | — | (a) |
| MPQB/Ethanol (T_A) | 41 | 47 | — | 16 | — | (b) |

Table 2 also shows the TDFS characteristic times of one other rigid polar probe, Coumarin 153 (Cu153) dissolved in various polar solvents, recently measured⁸ by Fleming *et al.*

Similar to MPQB, Cu153 has a higher dipole moment in the excited state than in the ground state and may form excited solute–solvent H-bonds in alcohols.⁸ The authors defined the TDFS of Cu153 as the time evolution of the first moment (the average frequency) of the whole emission spectrum of the probe.⁸ According to this definition, the authors show that, in all the studied solvents, the main part of the TDFS of Cu153 belonging to the picosecond time scale is unambiguously described by a biexponential law with characteristic times τ_1 (long) and τ_2 (short).⁸

For aprotic solvents (PC), the short characteristic time, τ_2 , is inside the experimental time resolution while the long time, τ_1 , is in the range of τ_M , as observed¹³ in the study of the TDFS of MPQB in such solvents.

For alcohol solvents it's obvious that the TDFS of Cu153, as defined in,⁸ integrates all the possible solvent effects; the red shift of a principal band, due to the “pure” solvent relaxation process, and the growing in of a new emission band, related to hydrogen bonded-complex formation, as shown above in the case of MPQB in alcohols. In these solvents, Fleming *et al.* observed two main characteristic times (see *Table 2*) which are well correlated to τ_M (τ_1 , the longer) and τ_L (τ_2 , the shorter). From these observations, we may assign, in Cu153, the slow characteristic time, τ_1 (correlated to τ_M) to excited solute–solvent hydrogen bonded-complex formation, and the short characteristic time τ_2 to collective reorganization of the solvent cage around the excited Cu153 probe. Such an assignment is coherent with the same assignment and observations made on the TDFS of the MPQB probe, as shown above.

With these new experimental results, one can now examine the fact that hydrogen

bonded-complex formation may occur on a time scale in the τ_M range. That can be understood if we take into account the arguments which hold for strong interactions between polar excited solute and highly polar aprotic solvents.¹³ Indeed, in aggregated solvents such as alcohols, excited solute–solvent H-bond formation is only possible (and can be observable) if the newly created forces between the excited solute and the specific solvent molecule forming the complex are sufficiently strong to break the solvent–solvent H-bond(s) between this specific solvent molecule and the bulk molecules. Moreover, the H-bond formation process implies a radical local solvent molecule reorientation (single-particle process) due to the highly specific geometries of the H-bond. Because this does not result from the macroscopic polarization of the dielectric medium implying collective reorientation of many solvent molecules (the dynamics of which occur in the τ_L range, as shown above), this specific solute-solvent phenomenon (H-bond formation) may lead to the observation of the solvent microscopic (single-particle) reorientation time τ_M in the time evolution of the emission spectrum of probes such as MPQB and Cu153 dissolved in solvents such as alcohol. Nevertheless, exact determination of the dynamics of H-bond formation from TDFS experiments strongly depends on the influence of this process on the emission spectrum of a given probe, as explained above in the case of MPQB and Cu153.

In many cases, such picosecond studies seem to reveal the presence of additional fast processes not observable with our experimental time resolution. Indeed, the amplitude $\delta\tilde{\nu}_{EM}$ (see *Table 1*) of the TDFS of MPQB associated with the longitudinal polarization of the solvent (described by τ_L) does not seem sufficient to account for the full amplitude of the non-specific solvation process ($\approx 2000\text{ cm}^{-1}$) as observed, for example, in *n*-Propanol at -75°C as shown in Figure 3. This is especially true in Methanol and Ethanol (see *Table 1*). This observation may be put together with the detection of a third (ultra-short) characteristic time (τ_3) in the TDFS of Cu153,⁸ as reported in *Table 2*. This ultrafast process may be tentatively ascribed to two possible mechanisms:

- 1) Polarization diffusion^{46–48} due to collective translational motion of the solvent molecules, which was predicted to be very fast (well under the τ_L range) and markedly efficient in small alcohols such as Methanol;⁴⁷ and/or
- 2) the coupling of the electronic excitation of the probe molecule with solvent high-frequency modes such as inertial oscillations of the solvent molecules (dipolarons²⁵, dipolar plasmons⁴⁹), which were recently shown^{25,49} to be strongly coupled to the longitudinal dielectric polarization of polar liquids as involved in solvation dynamics (the part of the solvation process scaled by τ_L).

Further work on a shorter time scale is obviously necessary in order to confirm such observations and to try to identify their origin.

V. CONCLUSION

A detailed examination of the experimental results^{7,8,13} and this work shows that *the hypothesis of two main relaxation mechanisms of polar solvents can quantitatively*

rationalize the low-frequency part of the solvation dynamics for three well characterized polar probes: MPQB, LDS-750 and Cu153, as studied by time resolved spectroscopy. These two mechanisms are:

- 1) The collective reorientation of solvent molecules in weak interaction with the probe, scaled by the (macroscopic) longitudinal relaxation time of the solvent (τ_L) as defined in Eq. (1);
- 2) the individual reorientation of the solvent molecules in strong interaction with the probe (including, tentatively, complex formation such as H-bonding), scaled by the microscopic (single-particle) solvent reorientation time (τ_M) as defined in Eq. (2).

Moreover, it may be seen that net solvation times (τ_S), as reported in other comparable studies¹⁰⁻¹² but following different procedures (without any systematic study of the influence of the possible different solute-solvent interactions on the observed spectra) fall generally in the limited range: $\tau_L < \tau_S < \tau_M$.

Considering the contrast between an increasing number of theoretical studies and the small number of well characterized experimental results on solvation dynamics in polar systems, one can emphasize that this study provides a simple and powerful way of understanding the essential features of this problem coherent with the actually available experimental results.

Thus, it has been shown here that solvation dynamics involves the macroscopic longitudinal polarization of the medium, scaled by τ_L (and perhaps involving some high-frequency modes of polar solvents) and, in highly interacting solute-solvent systems, the individual reorientation of solvent molecules, scaled by τ_M . Moreover, a rough examination of the nature and the range of the different interactions present in the medium (dipole-dipole, H-bonding, for example, as shown in this work) may be useful in order to detect the presence of the slow process (τ_M).

One believes that this contribution will help in furthering the understanding of more complex related problems in polar media (intramolecular processes such as electron-transfer and some other charge-transfer reactions, for example) by indicating how to scale the main (low-frequency) solvation dynamics using the known solvent times (τ_L , τ_M).

APPENDIX A

In the study of solvation dynamics it's of crucial importance to define precisely the physical quantities involved in the dielectric behaviour of polar solvents. Considering the wide variety of possible uses of the results of standard (frequency domain) dielectric loss measurements in polar liquids involved in solvation dynamics studies (see Ref.⁵⁰, for example), it is convenient to explain the choice of parameters, in this Appendix.

The dynamics of the orientational polarization of a polar solvent upon weak electric excitation (absence of dielectric saturation) is generally described by: $\epsilon(\Omega)$, the complex dielectric response function of the medium (as a function of the

excitation angular frequency Ω); ϵ_0 , the low-frequency limit (static) dielectric constant; ϵ_∞ , the high-frequency limit of $\epsilon(\Omega)$. The pure electronic polarization is described by the optical dielectric constant, n^2 , where n is the optical refraction index of the solvent. In real polar solvents, the measured values of the imaginary part of $\epsilon(\Omega)$ ($I_m\{\epsilon(\Omega)\}$) as a function of the real part ($Re\{\epsilon(\Omega)\}$) can be represented by the points (.) or (o) shown in Figure 5. These dispersion curves may be described by many analytical forms, as shown in Figure 5. Curve(1), the Debye form: $(\epsilon(\Omega) - \epsilon_\infty) = (\epsilon_0 - \epsilon_\infty)/1 - i\Omega\tau_D$, where the bulk dielectric relaxation time τ_D is determined from the frequency f_c at the maximum value of $I_m\{\epsilon(\Omega)\}$ as $2\pi f_c\tau_D = 1$.¹⁷ Curve(2), a superposition of many Debye regions associated with a discrete distribution of relaxation times in the medium.³¹ Curve(3), some others associated with a continuous distribution of relaxation times.^{32,33} In general the value of the infinite frequency limit ϵ_∞ , as deduced by extrapolation from such analytical forms of $\epsilon(\Omega)$, is found to be larger than n^2 , which was ascribed to such effects as atomic polarization.¹⁷ But none of the theoretical models leading to such analytical forms of dispersion curves explicitly treated intermolecular solvent-solvent interactions between polar solvent molecules.

Recently, Madden and Kivelson²⁵ showed (as previously mentioned by Lobo *et al.*⁴⁹) that some high-frequency modes such as librational oscillations may strongly affect the high-frequency part (HF) of the dispersion curves of polar solvents, as shown in curve(4) of Figure 5, leading to $\epsilon_\infty = n^2$. Using this model, it was shown²⁵ that the asymptotic low-frequency (LF) part ($\Omega \rightarrow 0$) of the dielectric response is given by a pure Debye form, as shown in curve(5) of Figure 5. Recently the (macroscopic) solvent dielectric relaxation time, τ_D , as determined from this low-frequency part of the dispersion curves was associated²⁵ with the microscopic (single-particle) reorientation time, τ_M , following Eq. (2) of the main text. This theoretical work sheds a new light on the old and ambiguous problem of the treatment of dielectric phenomena. In its present form, it does not try to explain all the observations made in real polar liquids. Nevertheless, it has been shown to be

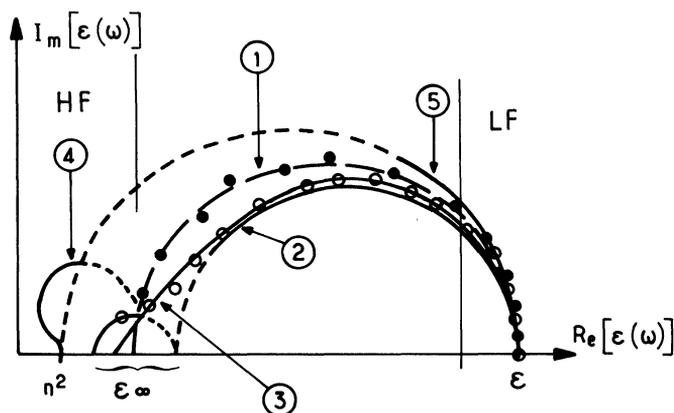


Figure 5 Different types of dispersion curves in polar liquids.

Table 3 Comparison between the molecular reorientation time (τ) as obtained from Molecular Dynamics simulations²⁹ and the microscopic reorientation time (τ_M) as calculated from Eq. (2), according to the theoretical models of dielectric phenomena,²⁵ in Methanol at different temperature

| $T(K)$ | $\tau(ps)$ | $\tau_M(ps)$ |
|--------|------------|--------------|
| 265 | 20.0 | 25.0 |
| 300 | 10.0 | 12.0 |
| 340 | 5.0 | 5.5 |

able to describe such high-frequency structures as curve(4) in Figure 5, and the results observed in simple liquids such as CHCl_3 .²⁵

Recent Molecular Dynamics (MD) simulations in Methanol²⁹ show molecular (single-particle) reorientation times, τ , in good agreement (Table 3) with the microscopic reorientation time, τ_M , as calculated from the set of dielectric data: $\{\epsilon_0, \epsilon_\infty = n^2, g_K (>1 \text{ in the case of Methanol}), \tau_D\}$ according to the theoretical models.²⁵

All of these considerations lead one to characterize a polar solvent by a set of data $\{\epsilon_0, \epsilon_\infty = n^2, g_K, \tau_D\}$, which allows one to calculate the microscopic reorientation time, τ_M , using Eq. (2), and the longitudinal relaxation time, τ_L , using Eq. (1). The above determination of τ_D from the low-frequency part of the dispersion curves (described by the pure Debye form: $(\epsilon(\Omega) - n^2) \rightarrow (\epsilon_0 - n^2)/(1 - i\Omega\tau_D)$ for $\Omega \rightarrow 0$) leads to numerical values of τ_D close to the generally reported values of the bulk dielectric relaxation time as determined from the currently used analytical expressions which describe the main part of the dispersion curves. This may be understood from Figure 5 where one observes that different analytical forms of $\epsilon(\Omega)$ equally well describe the LF region ($\Omega \rightarrow 0$). Thus, it's possible, in the absence of knowledge of the numerical values of $\text{Im}\{\epsilon(\Omega)\}$ and $\text{Re}\{\epsilon(\Omega)\}$ for a given solvent, to use the reported values of the bulk dielectric relaxation time of the solvent without significant error.

In conclusion of this brief comment on dielectric phenomena involved in solvation dynamics, one notes that the good agreement between the calculated values of the solvent characteristic times, τ_L and τ_M , from the set of data: $\{\epsilon_0, \epsilon_\infty = n^2, g_K, \tau_D\}$ and the measured values of the experimental characteristic times of TDFS of polar probes, as well as the values obtained from MD simulations as shown in Table 3, may be indirectly interpreted as arguments in favor of these theoretical models of dielectric phenomena.

References

1. W. R. Ware, S. K. Lee, G. J. Brant and P. P. Chow, *J. Chem. Phys.* **54**, 4729 (1971).
2. A. Declémy, C. Rullière and Ph. Kottis, *Chem. Phys. Lett.* **101**, 401 (1983).
3. S. W. Yeh, L. A. Philips, S. P. Webb, L. F. Buhse and J. H. Clark. *Ultrafast Phenomena IV*, edited by D. H. Auston and K. B. Eisenthal, Springer-Berlin, 359 (1984).

4. S. W. Yeh, Ph.D. thesis, Lawrence Berkeley Laboratory, University of California, LBL-20662 (1985).
5. C. Rullière, A. Declémy and Ph. Kottis, *Ultrafast Phenomena V*, edited by G. R. Fleming and A. E. Siegman, Springer-Berlin, 312 (1986).
6. A. Declémy, C. Rullière and Ph. Kottis, *Chem. Phys. Lett.* **133**, 448 (1987).
7. E. W. Castner, Jr, M. Maroncelli and G. R. Fleming, *J. Chem. Phys.* **86**, 1090 (1987).
8. M. Maroncelli and G. R. Fleming, *J. Chem. Phys.* **86**, 6221 (1987).
9. V. Nagarajan, A. M. Brearley, T. J. Kang and P. F. Barbara, *J. Chem. Phys.* **86**, 3183 (1987).
10. M. A. Kahlou, T. J. Kang and P. F. Barbara, *J. Phys. Chem.* **91**, 6452 (1987).
11. J. D. Simon and S. G. Su, *J. Chem. Phys.* **87**, 7016 (1987).
12. S. G. Su and J. D. Simon, *J. Phys. Chem.* **91**, 2693 (1987).
13. A. Declémy and C. Rullière, *Chem. Phys. Lett.* **146**, 1 (1988).
14. Yu. T. Mazurenko, *Opt. Spectrosc.* **36**, 283 (1974).
15. B. Bagchi, D. W. Oxtoby and G. R. Fleming, *Chem. Phys.* **86**, 257 (1984).
16. G. van der Zwan and J. T. Hynes, *J. Phys. Chem.* **89**, 4181 (1985).
17. H. Fröhlich, *Theory of Dielectrics*, Oxford University Press (1958).
18. D. F. Calef and P. G. Wolynes, *J. Chem. Phys.* **78**, 4145 (1983).
19. P. G. Wolynes, *J. Chem. Phys.* **86**, 5133 (1987).
20. R. F. Loring and S. Mukamel, *J. Chem. Phys.* **87**, 1272 (1987).
21. I. Rips, J. Klafter and J. Jortner, *J. Chem. Phys.* **89**, 4288 (1988).
22. T. Kakitani and N. Matage, *Chem. Phys. Lett.* **124**, 437 (1986).
23. D. M. Zeglinski and D. H. Waldeck, *J. Phys. Chem.* **92**, 692 (1988).
24. M. J. Kamlet, Ch. Dickinson and R. W. Taft, *Chem. Phys. Lett.* **77**, 69 (1981).
25. P. Madden and D. Kivelson, *Adv. Chem. Phys.* **56**, 467 (1984).
26. H. E. Lessing and M. Reichert, *Chem. Phys. Lett.* **46**, 111 (1977).
27. W. Dannhauser and L. W. Bahe, *J. Chem. Phys.* **40**, 3058 (1964).
28. V. Friedrich and D. Kivelson, *J. Chem. Phys.* **86**, 6425 (1987).
29. M. Haughney, M. Ferrario and I. R. McDonald, *J. Phys. Chem.* **91**, 4934 (1987).
30. W. L. Jorgensen, *J. Phys. Chem.* **90**, 1276 (1986).
31. S. K. Garg and C. P. Smith, *J. Phys. Chem.* **69**, 1294 (1965).
32. K. S. Cole and R. H. Cole, *J. Chem. Phys.* **9**, 341 (1941).
33. D. W. Davidson and R. H. Cole, *J. Chem. Phys.* **19**, 1484 (1951).
34. J. L. Salefran, C. Marzat and G. Vicq, *Adv. Mol. Relax. Inter. Proc.* **19**, 97 (1981).
35. J. A. Saxton, R. A. Bond, G. T. Coats and R. M. Dickinson, *J. Chem. Phys.* **37**, 2132 (1962).
36. D. Bertolini, M. Cassettari and G. Salvetti, *J. Chem. Phys.* **78**, 365 (1983).
37. D. J. Denney and R. H. Cole, *J. Chem. Phys.* **23**, 1767 (1955).
38. M. W. Sagal, *J. Chem. Phys.* **36**, 2437 (1962).
39. F. X. Hassion and R. H. Cole, *J. Chem. Phys.* **23**, 1756 (1955).
40. R. H. Cole and D. W. Davidson, *J. Chem. Phys.* **20**, 1389 (1952).
41. A. M. Bottereau, Y. Dutuit and J. Moreau, *J. Chem. Phys.* **66**, 3331 (1977).
42. *Handbook of Chemistry and Physics*. Ed. R. C. Weast (52d Ed). (1971–1972).
43. S. J. Bass, W. I. Nathan, R. N. Meighan and R. H. Cole, *J. Phys. Chem.* **68**, 509 (1964).
44. C. Rullière, A. Declémy and Ph. Pée, *Rev. Phys. Appl.* **18**, 347 (1983).
45. S. Besnainou, R. Prat and S. Bratoz, *J. Chim. Phys.* **61**, 222 (1964).
46. G. van der Zwan and J. T. Hynes, *Physica*, **121A**, 227 (1983).
47. G. van der Zwan and J. T. Hynes, *Chem. Phys. Lett.* **101** 367 (1983).
48. P. J. Stiles and J. B. Hubbard, *Chem. Phys.* **84**, 431 (1984).
49. R. Lobo, J. E. Robinson and S. Rodriguez, *J. Chem. Phys.* **59**, 5992 (1973).
50. E. W. Castner, G. R. Fleming and B. Bagchi, *Chem. Phys. Lett.* **143**, 270 (1980). It seems that a slight error got in this work, by defining τ_D as (l/ϵ_c) instead of $1/2\pi\epsilon_c$ from dielectric loss measurements in Ethylene-Glycol.³⁴