# High Electric Fields Elucidate the Hydrogen-Bonded Structures in 1-Phenyl-1-Propanol

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#### **Abstract**

High electric fields are applied to illuminate the role of hydrogen bonding in the dielectric relaxation of 1-phenyl-1-propanol (1P1P). Unlike many other monohydroxy alcohols, 1P1P is not associated with a strong distinct Debye loss peak, which would indicate chain-like hydrogen-bonded structures. We exploit the feature that high fields will enhance the dielectric constant, provided that ring-like (nonpolar) and chain-like (polar) structures exist in thermodynamic equilibrium. This so-called 'chemical effect' rests on a field-induced lowering of the free energy of the more polar species, thus shifting the equilibrium towards a higher dielectric constant. We demonstrate that an external electrical field of  $E_{\rm B} = 245\,{\rm kV\,cm^{-1}}$  increases the amplitude of the Debye peak, whereas that of the remaining loss profile remains constant. This indicates the coexistence of chain-like and less polar structures in supercooled 1P1P and helps to discriminate the Debye process from the signature of the primary structural relaxation.

Keywords: Dielectric, Hydrogen-bonding, Alcohol, Glass

#### 1. Introduction

Hydrogen-bonding in monohydroxy alcohols (MAs) causes the formation of transient supramolecular structures [1]. It is thus not surprising that the dynamics observed by dielectric relaxation in MAs differ from those of simple liquids, which has been observed early on [2, 3]. Regardless, the prominent dielectric loss peak typical of MAs has long been understood as the signature of the primary structural relaxation and referred to as  $\alpha$  process. For the case of 1-propanol, combined dielectric and photon correlation spectroscopy (PCS) studies have revealed that the structural relaxation coincides with a faster process with low intensity, not with the slowest Debye-like process that carries about 95 % of the total dielectric relaxation amplitude [4, 5]. This peak assignment was confirmed for 2-ethyl-1-hexanol (2E1H) on the basis of calorimetry [6], a case for which the Debye and  $\alpha$  processes are separated in frequency position by about 3.5 decades. More recent evidence suggests that the Debye peak is the result of the end-to-end vector fluctuations of transient chain-like structures, leading to an almost purely exponential or Debye-like dielectric relaxation in many MAs [7, 8].

Some MAs appear to display a single, asymmetrically broadened dielectric loss peak with no obvious indication of distinct processes. Examples for such behavior are 1-ethanol [9, 10, 11, 12] and 1-phenyl-1-propanol (1P1P) [13], where the dielectric relaxation is reminiscent of the dynamics of simple liquids without hydrogen bonding. In the case of 1P1P, it has been argued that the phenyl ring sterically hinders the formation of H-bonds [13], thus explaining the assumed absence of a Debye type process. According to a combined PCS and dielectric study of 1P1P, it is reasonable to separate the dielectric loss profile into an  $\alpha$  and a Debye relaxation component [14]. In this case, the  $\alpha$  process is about one decade faster than the Debye

relaxation, its amplitude is weaker and its loss peak is slightly broadened.

For many MAs, the static dielectric constant,  $\epsilon_s$ , is higher than what is expected on basis of the molecular dipole moment,  $\mu$ , and density using the Onsager relation [15]. This enhancement is the result of orientational correlations, which are disregarded in Onsager's treatment, and are quantified by the Kirkwood correlation factor  $g_K$ , which introduces an effective dipole moment,  $\mu_{\rm eff}$ , according to [16, 17]

$$g_{\rm K} = \frac{\mu_{\rm eff}^2}{\mu^2} = 1 + z \langle \cos \theta \rangle. \tag{1}$$

This correlation is often expressed in terms of the average number of neighbors, z, and the average orientation of neighboring dipoles,  $\langle \cos \theta \rangle$ . Relative to a lack of correlations, where  $g_{\rm K}=1$ , a value of  $g_{\rm K}>1$  indicates a preference for parallel dipole alignment and thus an increase in  $\epsilon_s$ , whereas  $g_K < 1$ points to anti-parallel dipole alignment and a reduction in  $\epsilon_s$ . In MAs such as 1-propanol, H-bonding results predominantly in chain-like structures, with a concomitant preference for parallel dipole alignment and thus high values of  $g_K$ . Some MAs, however, display a strong preference for forming ring-like structures, e.g., 3-methyl-3-heptanol [18], leading to very small values of  $g_K$ . For supercooled 1P1P, the value of  $g_K$  is near unity and increases slightly with decreasing temperature [19]. The situation of  $g_{\rm K} \approx 1$  can be interpreted either as largely uncorrelated dipole orientations or as a coexistence of chains with  $g_{\rm K} > 1$  and rings with  $g_{\rm K} < 1$ .

For example, 5-methyl-3-heptanol (5M3H) represents a case for which  $g_{\rm K}$  changes from 1.5 to 0.5 within a 20 K interval in the supercooled regime [18]. This is understood as the coexistence of rings and chains, with the equilibrium constant changing significantly with a 10% change in temperature. This im-

plies that ring- and chain-like structures have similar free energies, and suggests that an external electric field could be capable of modifying this equilibrium constant. This field effect has been verified experimentally by observing a field induced enhancement of the static dielectric constant [8, 20]. Therefore, experiments at high fields can discriminate between the two scenarios leading to  $g_K$  values near unity: a lack of orientational dipole correlation, or a mixture of ring- and chain-like structures with volume fractions such that the average effective dipole moment is approximately equal to the molecular dipole moment.

In this work, we employ static high electric fields to demonstrate that the value of  $g_K$  for supercooled 1P1P is the result of a thermodynamic equilibrium of species of different polarity, *i.e.*, of chains and rings or chains and uncorrelated dipoles. We observe that high fields enhance the dielectric amplitude of only the Debye component of the loss spectrum, consistent with the idea of a field induced shift towards more chain-like H-bonded structures. Moreover, the result justifies the partitioning of the dielectric loss spectrum into a Debye and  $\alpha$  relaxation component, as is typical for MA type liquids.

## 2. Experiment

1-phenyl-1-propanol was purchased from TCI with a purity > 98.0 % and used as received. Low field measurements were performed in the regime of linear response to obtain a detailed characterization of the dielectric relaxation of the present sample. The resulting data are also used to calibrate the electrode spacing of the high field cell.

For the low field dielectric experiments, an Invar plate capacitor with electrode separation of about  $80\,\mu m$  was used [21]. The measurements were performed by a Solartron Instruments SI-1260 impedance - gain/phase analyzer with a DM-1360 interface. The system was calibrated by measuring the empty Invar cell. The excitation voltage is set to 1 V, resulting in a peak field strength of  $0.18\,k V$  cm<sup>-1</sup>. A Novocontrol Quatro cryo system is employed for temperature control.

Details of the high field setup have been described previously [20]. The capacitor consists of two spring-loaded polished stainless steel electrodes with diameters 17 mm and 20 mm, separated by a 25 µm thick Kapton ring with an inner sample area of 14 mm diameter. The capacitance contribution from the Kapton ring is subtracted from all data. The cell is mounted onto the cold stage of a closed cycle He-refrigerator cryostat, with a Lakeshore Model 340 unit stabilizing the temperature within several mK. High dc bias field experiments are performed using a Solartron 1260 gain/phase analyzer, combined with a Trek PZD-350 high-voltage amplifier. The current is recorded as the voltage drop across an RC network acting as shunt with an impedance that rises with decreasing frequency from  $250\,\Omega$  (at  $10^4\,\mathrm{Hz}$ ) to  $300\,\mathrm{k}\Omega$  (at 1 Hz). The signal is accoupled (RC = 0.12 s) to a buffer amplifier that protects the system from consequences of sample failure. For each frequency, the system is programmed to perform 3 measurements with the bias field  $E_{\rm B}$  on, followed by 5 measurements with no bias field (with an ac field with RMS amplitude of 20 % of  $E_{\rm B}$  applied

during all measurements). Each acquisition process integrates the signal for the greater of 1 s or 8 periods. This protocol is designed to capture steady-state impedance values at the high bias fields, while avoiding exposure to high fields for excessive times and providing sufficient recovery time between high field measurements.

#### 3. Results

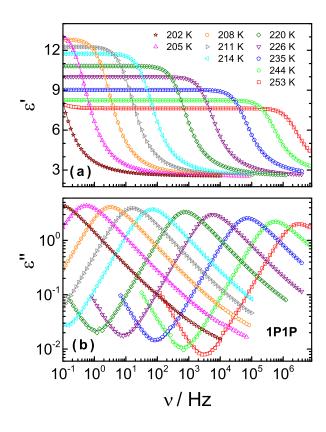


Figure 1: Low field dielectric permittivity (a) and loss (b) spectra of 1P1P for selected temperatures. The lines are fits as given by Eq. 3.

To gain access to the dielectric behavior of supercooled 1P1P, low field measurements were performed for frequencies,  $\nu$ , in the range from 0.1 Hz to 10 MHz. The spectra for selected temperatures, T, are shown in Fig. 1. At all T, a dominant dielectric relaxation process is reflected in the curves by a step-like decrease of the permittivity,  $\epsilon'$ , from  $\epsilon_s$  at low frequencies to  $\epsilon_{\infty}$  at high  $\nu$ , accompanied by a peak in the loss,  $\epsilon''$ . With increasing T, these features move to higher frequencies, with the peak frequency  $v_{\text{max}}$  shifting from 0.5 Hz at 205 K to 3.3 MHz at 253 K. Over the same temperature range, the static permittivity decreases from 13 to 7.6, while  $\epsilon_{\infty} = 2.6$  remains constant. The loss peaks are characterized by a low-frequency flank with  $\epsilon'' \propto v^{+1}$ , but a less steep high-frequency slope, indicating the asymmetric broadening typical of supercooled liquids. For  $T \ge 220 \,\mathrm{K}$ , at frequencies below the main peak, an additional contribution to the loss  $(\epsilon'' \propto \nu^{-1})$  appears due to dcconductivity,  $\sigma_{dc}$ , in the sample.

Close examination of the high-frequency flanks of the main peak reveals a slight, wing-like contribution (e.g., for 220 K at  $v \gtrsim 100\,\mathrm{kHz}$ ), indicating a second relaxation process superimposed onto the main peak. For the lowest temperatures, a further relaxation process is indicated by an additional wing at higher v, e.g., for the 202 K-curve at  $v > 1\,\mathrm{kHz}$ . This third process is probably related to the  $\beta$ -relaxation and will not be discussed further in this paper [19]. As detailed below, an attempt to fit the loss peak with a single Cole-Davidson (CD) function [22],

$$\epsilon^*(\omega) = \epsilon_{\infty} + \frac{\Delta \epsilon}{(1 + i\omega \tau)^{\beta}},$$
 (2)

did not yield satisfactory results. Here,  $\omega=2\pi\nu$  is the angular frequency,  $\Delta\epsilon=\epsilon_{\rm s}-\epsilon_{\infty}$  the relaxation strength,  $\tau$  the relaxation time and  $0<\beta\leq 1$  the asymmetric broadening parameter, with  $\beta=1$  representing the Debye case with no broadening.

In order to account for the superposition of two processes, a Debye-like relaxation and an  $\alpha$ -peak, we employ a fitting function given by the sum of two CD components and an additional term to account for the dc-conductivity:

$$\epsilon^*(\omega) = \epsilon_{\infty} + \frac{\Delta \epsilon_{\rm D}}{(1 + i\omega \tau_{\rm D})^{\beta_{\rm D}}} + \frac{\Delta \epsilon_{\alpha}}{(1 + i\omega \tau_{\alpha})^{\beta_{\alpha}}} + \frac{\sigma_{\rm dc}}{\epsilon_0 \omega}, \quad (3)$$

where  $\epsilon_0$  is the vacuum permittivity. The small spectral separation of the two peaks requires careful fitting of the measured data in order to extract the characteristic properties of both relaxations. For this purpose, simultaneous fits of the real and imaginary part of  $\epsilon^*$  have been performed for all temperatures.

The individual components derived from fitting with Eq. 3 are exemplarily shown for 220 K in Fig. 2(a). It can be seen that the separation between the Debye and  $\alpha$  peaks is less than a decade. At this temperature,  $\Delta \epsilon_D = 6.4$  is more than three times higher than  $\Delta \epsilon_{\alpha} = 1.8$ . However, while a constant  $\beta_{\rm D} = 0.91$  was assumed, the structural peak is more broadened  $(\beta_{\alpha} = 0.43)$ , resulting in a visible wing at the highest frequencies. It should be emphasized that fits with only a single CDcomponent (as well as the  $\sigma_{dc}$  term) do not appropriately describe the data. This is visualised in Fig. 2 (b). Here, the relative difference, i.e.,  $(\epsilon''_{\text{meas}} - \epsilon''_{\text{fit}})/\epsilon''_{\text{meas}}$ , between measured and fitted data is shown for both approaches. It becomes obvious that a single CD-component can suitably describe the low-frequency flank, but deviates significantly from the measurement close to the peak ( $v \approx 1 \text{ kHz}$ ) and on the high-frequency flank. In particular, it fails to account for the  $\alpha$ -wing ( $\nu \gtrsim 200 \, \text{kHz}$ ).

The entire dielectric spectra are captured satisfactorily with the model given by Eq. 3 for all temperatures, as shown for selected T by the lines in Fig. 1 (a) and (b). It can be seen that they coincide very well with the measurements, with the exception of the  $\beta$  relaxation at low T and high  $\nu$ , and a slight increase in  $\epsilon'$  at the lowest frequencies of the 253 K-curve, which can be attributed to electrode polarisation. We find that the increase in  $\epsilon_s$  observed upon temperature reduction can be attributed solely to an increase of  $\Delta\epsilon_D$  from 3.7 at 253 K to 8.8 at 202 K, while  $\Delta\epsilon_{\alpha}\approx 1.9$  and  $\epsilon_{\infty}=2.5$  show no systematic T dependence. The same is true for the broadening parameter ( $\beta_{\alpha}\approx 0.43$ ).

The temperature dependence of the relaxation times is depicted in Fig. 3. Here, we show the average relaxation times

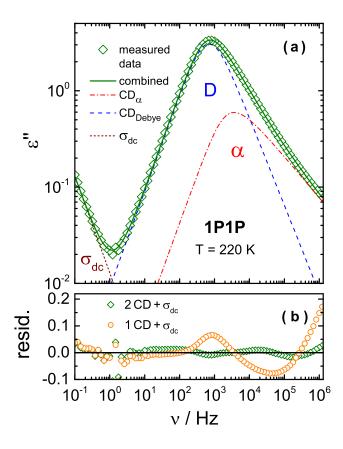


Figure 2: (a) Fitting components as employed in Eq. 3 for one exemplary spectrum at T = 220 K. (b) Deviation of fits from measured data for a fit according to Eq. 3 (dark green) and for the best fit with only one CD component (orange).

 $\langle \tau \rangle = \beta \cdot \tau$  with  $\beta$  and  $\tau$  obtained by the fits as described above. Our results are in good agreement with those recently obtained by Böhmer *et al.* by combining broadband dielectric spectroscopy (BDS) and light scattering experiments [19]. The super-Arrhenius T dependence can be described appropriately with the empirical Vogel-Fulcher-Tammann (VFT) equation [23, 24, 25]:

$$\tau = \tau_{\infty} \cdot \exp\left(\frac{D \cdot T_{\rm VF}}{T - T_{\rm VF}}\right). \tag{4}$$

Here,  $\tau_{\infty}$  denotes the relaxation time at very high T, D is the strength parameter quantifying the deviation from Arrhenius behavior, and  $T_{\rm VF}$  the Vogel-Fulcher temperature. In accordance with previous findings [19], we observe a nearly constant separation of the relaxation times over the full temperature window ( $\tau_{\rm D}/\tau_{\alpha}\approx 6$ ). Accordingly, the liquid fragility parameters [26] for the Debye and  $\alpha$  relaxation times are nearly identical (m=72 and 76, respectively). We find a glass temperature, defined as the temperature where  $\tau_{\alpha}=100\,{\rm s}$ , of  $T_{\rm g}=194.6\,{\rm K}$ . The equivalent temperature for the Debye relaxation time  $T(\tau_{\rm D}=100\,{\rm s})=T_{\rm g}({\rm D})$  is 196.9 K.

As detailed in the experimental section, the effects of high electric fields have been recorded by alternating between low and high field during a frequency sweep, thus generating one

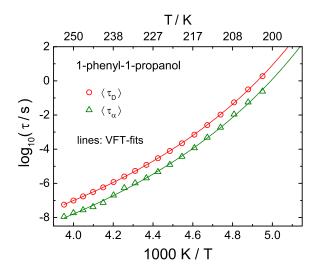


Figure 3: Arrhenius plot of the average relaxation times  $\langle \tau_{\alpha} \rangle$  and  $\langle \tau_{D} \rangle$ . The lines are VFT-fits according to Eq. 4.

spectrum that is practically equivalent to the low field limit, and one that is measured while a dc bias field of  $E_{\rm B}=245\,{\rm kV\,cm^{-1}}$  is applied. Such data have been acquired for temperatures between 220 K and 211 K, and the low field results for  $\epsilon'$  and  $\epsilon''$  are shown in the upper plots labeled (a) of Fig. 4 and 5, respectively. In order to visualize the small field-induced changes, we calculate the relative change of permittivity between the high and low field case, but with  $\epsilon_{\infty}$  subtracted because its value is practically field invariant. Accordingly, the high field results are illustrated for the storage component in terms of  $(\epsilon'_{\rm hi}-\epsilon'_{\rm lo})/(\epsilon'_{\rm lo}-\epsilon_{\infty})$  in Fig. 4 (b) and for the loss component as  $(\epsilon''_{\rm hi}-\epsilon''_{\rm lo})/\epsilon''_{\rm lo}$  in Fig. 5 (b).

At low frequencies, the field effect on the real part of permittivity amounts to an increase of the dielectric relaxation amplitude  $\Delta\epsilon$  by about 3%, see Fig. 4(b). This is indicative of the so-called 'chemical effect' [27]. Towards higher frequencies, the relative change of  $\epsilon' - \epsilon_{\infty}$  becomes negative, consistent with the loss peak being shifted to lower frequencies. The relative change of  $\epsilon''$  varies from 8% to -1% with increasing frequency, see Fig. 5(b). The orange lines in these figures represent the results of a model outlined below.

## 4. Discussion

The effect of hydrogen bonding on the structure and dynamics of liquids has been a topic of intense research activities. This is particularly true for MAs, which are known to be associated with supramolecular structures [1]. In the case of H-bonded chain-like topologies, the resulting parallel dipole alignment leads to enhanced Kirkwood correlation factors ( $g_K > 1$ ) and static dielectric constants,  $\epsilon_s$ , and in many cases to a prominent Debye-type signature in the dielectric relaxation spectrum. The molecular structure of some MAs induces a preference for ring-like topologies resulting in  $g_K < 1$ , low  $\epsilon_s$ , and Debye processes with small or negligible amplitude. The situation of  $g_K$  near unity is more ambiguous, because both uncorrelated dipoles as

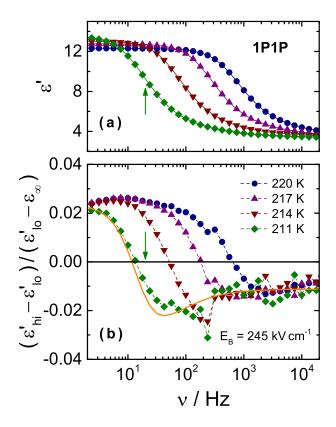


Figure 4: Effect of a dc bias field with amplitude  $E_{\rm B}=245\,{\rm kV\,cm^{-1}}$  on the dielectric permittivity of 1P1P for temperatures between 220 K and 211 K. (a) Low field permittivity spectra ( $E_{\rm B}=0$ ), (b) the relative difference between high ( $\epsilon_{hi}$ ) and low ( $\epsilon_{lo}$ ) bias field permittivity, quantified in terms of ( $\epsilon'_{\rm hi}-\epsilon'_{\rm lo}$ )/( $\epsilon'_{\rm lo}-\epsilon_{\infty}$ ). Arrows mark the loss peak frequency position for  $T=211\,{\rm K}$ . The model leading to the solid orange curve is described in the text.

well as a mix of ring- and chain-like structures will explain a net value of  $g_{\rm K} \approx 1$ . The latter, however, is the situation with 1P1P, where  $g_{\rm K}$  decreases from 1.6 to 1.4 when the temperature is raised from 1.1  $T_{\rm g}$  to 1.2  $T_{\rm g}$  [19].

As has been demonstrated earlier for the MA 5M3H, a high electric dc field causes a 'chemical effect', *i.e.*, a field induced increase in  $\epsilon_s$  that demonstrates the coexistence of more and less polar species (chains and rings, respectively) in thermodynamic equilibrium. By contrast, 1-propanol with  $g_K \approx 3.5$  shows no such field effect [28]. In general, high field dielectric experiments are capable of discriminating between two scenarios leading to a certain Kirkwood factor: a strong thermodynamic preference for a structure associated with that  $g_K$ , or a mixture of two (or more) structures, one with higher and one with lower  $g_K$ . Naturally, the latter case of a mixture implies that the free energies of the species involved are similar, such that an electric field can modify the equilibrium constant.

The present results clearly identify an increase of the static dielectric constant with the application of an external electrical dc bias field. The effect amounts to +3% with respect to  $\Delta\epsilon$  for a field  $E_{\rm B}=245\,{\rm kV\,cm^{-1}},$  cf. the low frequency limit in Fig. 4 (b). However, the results for both  $(\epsilon'_{\rm hi}-\epsilon'_{\rm lo})/(\epsilon'_{\rm lo}-\epsilon_{\infty})$  and

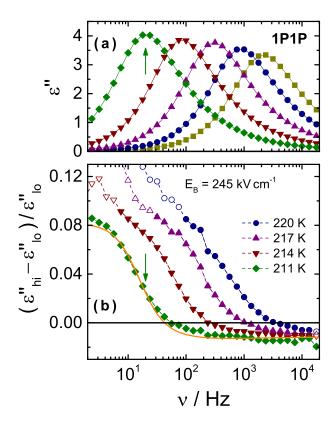


Figure 5: Effect of a dc bias field with amplitude  $E_{\rm B}=245\,{\rm kV\,cm^{-1}}$  on the dielectric loss of 1P1P for temperatures between 220 K and 211 K. (a) Low field loss spectra ( $E_{\rm B}=0$ ), (b) the relative difference between high ( $\epsilon_{hi}$ ) and low ( $\epsilon_{lo}$ ) bias field loss, quantified in terms of ( $\epsilon_{hi}'' - \epsilon_{lo}'')/(\epsilon_{lo}'')$ ). Open symbols indicate data affected by dc-conductivity. Arrows mark the loss peak frequency position for  $T=211\,{\rm K}$ . The model leading to the solid orange curve is described in the text.

 $(\epsilon_{hi}^{\prime\prime}-\epsilon_{lo}^{\prime\prime})/\epsilon_{lo}^{\prime\prime}$  reveal a significant frequency dependence of the percentage change, with both quantities evolving to negative values at the higher frequencies. Because it is assumed that the loss profile of 1P1P is the superposition of two processes, an amplitude increase that affects both loss peaks equally is not expected. Instead, the 'chemical effect' in MAs should enhance only the amplitude of the Debye process.

In order to quantify the field effect in more detail, we focus on the HN fit based on Eq. 3 and illustrated in Fig. 2, assuming field invariant values for  $\beta_{\rm D}$  and  $\beta_{\alpha}$ . This leaves the four parameters  $\Delta\epsilon_{\rm D},\,\Delta\epsilon_{\alpha},\,\tau_{\rm D},$  and  $\tau_{\alpha}$  as potentially changing with the application of an external field. The goal is to fit the relative difference data in Fig. 4 via  $(\epsilon'_{\rm hi}-\epsilon'_{\rm lo})/(\epsilon'_{\rm lo}-\epsilon_{\infty})$  and those in Fig. 5 via  $(\epsilon''_{\rm hi}-\epsilon''_{\rm lo})/\epsilon'_{\rm lo}$ . Here,  $\epsilon^*_{\rm lo}$  is calculated from Eq. 3 with the original low field parameters, while  $\epsilon^*_{\rm hi}$  is derived from the same fit function but with modified values for  $\Delta\epsilon_{\rm D},\,\Delta\epsilon_{\alpha},\,\tau_{\rm D},$  and  $\tau_{\alpha}$ .

The results of this approach are included as solid orange lines in Fig. 4(b) and Fig. 5(b) for the real and imaginary components of the permittivity, respectively. In the process of determining how the HN parameters change with field, it became clear that changing amplitudes and/or time constants equally

for the Debye- and  $\alpha$ -process does not lead to satisfactory results. Instead all four parameters,  $\Delta\epsilon_{\rm D}$ ,  $\Delta\epsilon_{\alpha}$ ,  $\tau_{\rm D}$ , and  $\tau_{\alpha}$ , required independent relative changes. A good fit for both the  $\epsilon'_{\rm hi}$  and  $\epsilon''_{\rm hi}$  was obtained by assuming the following percentage changes for a field of  $E_{\rm B}=245\,{\rm kV\,cm^{-1}}$ :  $\Delta\epsilon_{\rm D}$ :  $+3.0\,\%$ ,  $\Delta\epsilon_{\alpha}$ :  $+0.0\,\%$ ,  $\tau_{\rm D}$ :  $+5.3\,\%$ , and  $\tau_{\alpha}$ :  $+2.5\,\%$ . Two parameter changes can be derived directly from the percentage change curves for  $T=211\,{\rm K}$ :  $+3.0\,\%$  for  $\Delta\epsilon_{\rm D}$  is seen as low- $\nu$  limit in Fig. 4 (b), and  $+8.3\,\%$  for  $\Delta\epsilon_{\rm D}$  it self. At higher temperatures, the low frequency limits of  $(\epsilon''_{\rm hi}-\epsilon''_{\rm lo})/\epsilon''_{\rm lo}$  are obscured by dc-conductivity, as indicated by open symbols in Fig. 4 (b). The remaining two quantities,  $\Delta\epsilon_{\alpha}$  and  $\tau_{\alpha}$ , are then adjusted so that the fit captures the negative levels at around  $10^4\,{\rm Hz}$  and the frequency positions at which the field effect vanishes.

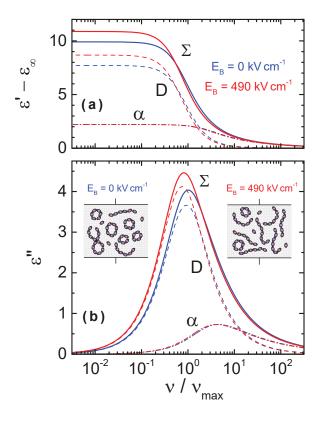


Figure 6: Theoretical influence dielectric spectra of high electrical dc fields (red) of  $490\,\mathrm{kV}\,\mathrm{cm}^{-1}$  compared to low fields (blue) on 1P1P. Debye (dashed lines) and  $\alpha$  (dashed-doted lines) relaxation contributions are separated and illustrate the increased shift and intensity by the electric field of the Debye relaxation. The left sketch illustrates the ring-chain equilibrium which is shifted to ring-like structures in the right sketch with an applied electric field. Chain structures have stronger relaxation and slower relaxation times compared to ring structures.

In order to better illustrate how a high electric field modifies the dielectric relaxation behavior, Fig. 6 displays two sets of curves calculated from the above fit results: one set for  $E_{\rm B} \approx 0\,{\rm kV\,cm^{-1}}$  and one for  $E_{\rm B} = 490\,{\rm kV\,cm^{-1}}$ , *i.e.*, for twice the experimental field so that the field induced differences are exaggerated by a factor of four relative to the experimental sit-

uation. One can observe that the field induced increase of the static dielectric constant is solely due to the Debye process. It is also evident that it is mainly the Debye process which is responsible for the overall shift of the loss peak to low frequencies. The cartoon-like insets are meant to emphasize that the high field curves are associated with a higher fraction of chain-like structures.

Our finding of the amplitude of solely the Debye process being enhanced by external dc fields is consistent with the picture that the balance of supramolecular structures is shifted towards more polar (chain-like) topologies. Thus, the result that only the Debye contribution to permittivity is subject to this 'chemical effect' is highly supportive of understanding the loss profile of 1P1P as the sum of two distinct contributions. The effect that a static electric field leads to larger time constants is typical for polar (non-H-bonding, H-bonding, MAs) supercooled liquids [29, 30, 31], but the change in topology may further amplify the slowing down of relaxation dynamics [20].

## 5. Summary and Conclusions

The aim of this study is to gain a deeper understanding of the role of hydrogen-bonding in the structure and dynamics of this MA, which does not allow for an obvious distinction of the Debye- and  $\alpha$ -processes typical for MA's. To this end, we have studied the effect of a high dc bias electric field on the dielectric relaxation of supercooled 1P1P. We observe that a field of  $E_{\rm B}=245\,{\rm kV\,cm^{-1}}$  induces an increase of the dielectric relaxation amplitude,  $\Delta\epsilon$ , and of the relaxation time constant,  $\tau$ . However, the loss profile is not affected in a uniform fashion. Instead, we find that the amplitude change (+3%) is limited to that of the Debye-like contribution,  $\Delta\epsilon_{\rm D}$ , while  $\Delta\epsilon_{\alpha}$  remains constant.

This field effect lends strong support to identifying the slower Debye-like contribution to permittivity as the process associated with the fluctuations of H-bonded structures, whereas the faster loss component reflects the structural ( $\alpha$ ) relaxation. The field effect on  $\Delta\epsilon_D$  also implies that the Kirkwood correlation factor  $g_K \approx 1.3$  originates from the coexistence of chain-like and less polar structures (e.g., rings or individual molecules), rather than from a thermodynamically strongly preferred single structure.

The work demonstrates that the addition of high static fields to dielectric spectroscopy is a powerful tool to elucidate the role of supramolecular structures in the structure and dynamics of monohydroxy alcohols and possibly other hydrogen bonded polar systems.

## 6. Acknowledgment

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