Non-rotational mechanism of polarization in alcohols

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Models following the widely used Debye’s phenomenological approach to dielectric relaxation aim to explain the frequency-dependent complex dielectric function. They assume rotational diffusion of the polar molecules and ad hoc dipole relaxation time models failing to cover the full dc up to THz spectral range. Here, using the illustrative case of monohydric alcohols, we show that intermolecular separation of excess protons and “proton-holes” in the polar liquid, governs its static and dynamic dielectric properties on the same footing. We performed systematic ultrabroadband (0-10 THz) spectroscopy experiments with monohydric alcohols of different (0.4-1.6 nm) molecular lengths; and we propose a model that accurately describes the dielectric response of all the studied alcohols across the entire frequency range, without any rotational diffusion mechanism nor the knowledge of a molecule’s dipole moment. This substantiates the proposed intermolecular polarization mechanism.

Introduction A polar liquid can be seen as a system of permanent electric dipoles interacting with one another. The frequency-dependent response of such a liquid to the perturbation of an oscillating electric field manifests itself via the dielectric relaxation. The interpretation of dielectric spectra yields information on the dipole relaxation time and mechanisms, which in turn provides a detailed understanding of the physical and chemical properties of polar liquids, including their molecular structures, interactions, and dynamics. Water and alcohols are two typical examples of polar liquids, but many more may be found in nature or synthesized. In particular, some chelate compounds like hemoglobin and chlorophyll play a vital role in biological systems, thus illustrating the importance of chemical polarity.

The polar character of alcohols is due to the presence of the characteristic hydroxyl group, −OH, bound to a carbon atom that forms simple covalent bonds with other groups of atoms. Just like water, alcohols have a relatively high dielectric constant and are good solvents. Their typical size and relatively low complexity make them interesting systems to study with dielectric spectroscopy. That is why over the past decades, the interaction of electric fields with alcohols has been the object of experimental and theoretical research [1–11], which showed many other fundamental similarities with water [12,13]. These findings notably triggered the studies of alcohols in the glassy state - an experimentally inaccessible thermodynamic region for water [14,15], which led to the prediction of some supercooled [16] and confined [17] water properties, as well as deeper insights into dielectric phenomena in protonic liquids [18]. However, the understanding on the microscopic level of the response of alcohol molecules to an alternating electric field remains far from complete [8,10,20].

Debye’s early phenomenological models of the dielectric polarization assumed molecules as rigid dipoles following the external electric field direction, with a characteristic time \( \tau \) reflecting the average effect of molecular correlations [21,22]. In Debye’s approach the parametric relationship between the real and imaginary parts of the dielectric function in Cole-Cole diagrams [22,23] differs from experimental data in the high-frequency domain, implying that important short-time scale physics is missed altogether. For alcohols, the discrepancy between the measured dielectric constants and those determined by calculation with the Debye formula using a molecular dipole moment value of \( \mu \approx 1.7 \) D becomes significant at low temperatures [26] because the Debye model does not account for temperature, steric, and entropic effects that influence the molecules’ geometry as shown with isomeric octanols [27].

In fact, knowledge of the dipole moment \( \mu \) of a single molecule is alone insufficient to explain the experimentally observed polarization of alcohols. One may consider a chain-like structure made of several −OH groups as the transient chain model for monohydric alcohols [3]. Then, if \( \mu = 1.7 \) D, the total of 6 aligned moments in a chain is \( \sim 10 \) D, which is large enough to account for the dielectric constant. Nonetheless, three problems remain: i/ there is no proton transfer in this chain model, hence no dc conductivity; ii/ the dielectric relaxation time is too short to allow for the alignment of a sizable number of dipoles [28]; iii/ the thermal energy \( k_B T = 0.026 \) eV is an order of magnitude larger than the dipole-dipole interaction energy \( E_{dd} = \mu^2/(4\pi\varepsilon_0\sigma^3) \sim 10^{-3} \) eV, with \( \varepsilon_0 \) being the vacuum permittivity, so no long-lived chain-like structures are possible in alcohols on the time scale of dielectric relaxation.

Accounting for intermolecular correlations and local-field effects [29,31], and using improved models for the relaxation time [32,34] yields good theory-experiment agreement for the dielectric constants of alcohols [18,35]. However, other dynamical processes, such as self-diffusion, protonic current, and high-frequency (tera-hertz) modes as well as their temperature dependen-
cies, still lack clarity [12] [34] [39] because the atomic and molecular dynamics, their time-dependent correlations, and relations between conductivity and mobility are all hidden in the dielectric response. In the present work, we perform a systematic ultra-broadband dielectric spectroscopy study on a series of monohydric alcohols of increasing carbon chain length. In comparison with previous studies [11] [18] [19], we expand the frequency domain from the static conductivity up to the terahertz range. From this data we propose a model which supports a single molecular mechanism as responsible for conductivity and dielectric polarization. Our model is based on the assumption of charge separation over intermolecular distances, i.e. the release of protons from the molecules because of quantum-mechanical tunneling [40], leading to the formation of “excess proton-proton hole” (protonic) dipoles. This mechanism yields the expected dipole moments and explains dc conductivity. As the protonic dipole moment does not depend on molecular orientation, there is no need to posit a particular intermolecular structure. The proposed polarization mechanism is diffusion-controlled.

**Experimental** We used as-received, commercially available high-purity (>99.9%) primary monohydric alcohols, which we classify according to their molecular length, characterized by the number of carbon atoms, \( n \), in their hydrocarbon chain: methanol, ethanol, 1-propanol, 1-butanol, and decanol \( (n = 1, 2, 3, 4, 10) \). We used commercial Keysight E4980A and N9917A impedance analyzers, operating in the parallel plate and coaxial probe modes, respectively. The real, \( \epsilon' \), and imaginary, \( \epsilon'' \), parts of the dielectric function were obtained following the standard procedure [41]. The sample temperature was controlled by Peltier elements within 0.3 K accuracy in the 283 - 363 K temperature range. The terahertz spectra were adapted from Refs. [12] [13]. In this way, we accumulated spectral data from 1 kHz to 10 THz.

Figure 1 shows our measurement data of the alcohols’ dielectric constants \( \epsilon'(\nu) \), dielectric losses \( \epsilon''(\nu) \), and dynamic conductivities \( \sigma(\nu) = 2\pi \epsilon' \nu \epsilon''(\nu) \). With molecular lengths ranging from 0.4 to 1.6 nm, the alcohol molecules stretch from almost spherical to rode-like geometries, retaining their dipole moment \( \mu \). The static dielectric constant, \( \epsilon'(0) \), direct-current conductivity, \( \sigma_{dc} \), high-frequency conductivity, \( \sigma_{\infty} \), relaxation time, \( \tau_r \), and terahertz vibrational frequency, \( \nu_0 \), are also shown in Fig. 1 and their values given in Table I. The time \( \tau_2 \) and \( \tau_1 \), again irrespective of the molecular aspect ratio (effective diameter/molecule length) for all alcohols considered in our work. This strongly suggests that the same microscopic mechanisms govern the dielectric losses for all alcohol studied. Note that the high-frequency wings \( E_1 \) and the dc conductivity (yellow and pink areas in Fig. 2), are also scaled. This implies that they are governed by a common molecular mechanism, which is the same for the main relaxation band \( R_1 \), again irrespective of the molecule geometries. Data accuracy for decanol is the object of a separate discussion [28].

Figure 2 shows part of the dielectric losses data of Fig. 1 in the 1 kHz to 0.1 THz range. For each \( n \) considered, the functions \( \epsilon''(\nu) \) are normalized to their corresponding maximum value \( \epsilon''_{max} \) of the relaxation \( R_1 \) at corresponding frequency \( \nu_1 \) given in Table I. All the normalized \( \epsilon''(\nu) / \epsilon''_{max} \) spectra collapse into a unique master curve irrespective of their molecular aspect ratio (effective diameter/molecule length) for all alcohols considered in our work. This strongly suggests that the same microscopic mechanisms govern the dielectric losses for all alcohol studied. Note that the high-frequency wings \( E_1 \) and the dc conductivity (yellow and pink areas in Fig. 2), are also scaled. This implies that they are governed by a common molecular mechanism, which is the same for the main relaxation band \( R_1 \), again irrespective of the molecule geometries. Data accuracy for decanol is the object of a separate discussion [28].

**FIG. 1.** Broadband dielectric-terahertz spectra of monohydric alcohols \( n = 1, 2, 3, 4, 10 \). The panels (a) and (b) display the real \( \epsilon' \) and imaginary \( \epsilon'' \) parts of the dielectric function; and (c) the dynamical conductivity \( \sigma \). Experimental data are represented by open circles; continuous lines result from our model. Colored areas and dashed lines are guides for the eyes.

**TABLE I.** Electrodynamic parameters of monohydric alcohols shown in Fig. 1.

| \( n \) | 1 | 2 | 3 | 4 | 10 |
|-------|---|---|---|---|----|
| \( \epsilon(0) \) | 34 | 26 | 22 | 19 | 8.5 |
| \( \sigma_{dc} (\mu\text{S}\cdot\text{m}^{-1}) \) | 57 | 37 | 12 | 7.4 | 0.13 |
| \( \sigma_{\infty} (\text{S}\cdot\text{m}^{-1}) \) | 4.77 | 1.22 | 0.41 | 0.24 | 0.027 |
| \( \tau_r (\text{ps}) \) | 54 | 177 | 370 | 549 | 1989 |
| \( \nu_1 (\text{GHz}) \) | 2.95 | 0.90 | 0.43 | 0.29 | 0.08 |
| \( \nu_0 (\text{THz}) \) | 2.89 | 2.57 | 2.39 | 2.20 | 2.05 |
| \( \tau_m (\text{ns}) \) | 16 | 30 | 80 | 122 | 937 |

Energy from 0.13 eV (methanol) to 0.27 eV (decanol) with
increasing $n$. All alcohols studied show nearly identical trends of increasing $\sigma_{dc}$ and $\sigma_\infty$. We also observe that for a given $n$, the activation energies are nearly the same when calculated from both the dc and high-frequency conductivity values (Table II). This property implies the same driving mechanism for both high- and low-frequency conductivities, which relates to self-diffusion of molecules. Note that the dc conductivities $\sigma_{dc}$ measured in this study are lower than those obtained in [46, 47]. Further, our data clearly show that the activation energies $E$ increase with $n$, whereas the previous studies reported a constant value $E = 0.16$ eV for all alcohols [46, 47]. This discrepancy may be caused by the different purity of samples: our samples have higher purity, and show consistent behavior of the conductivity, correlated with self-diffusion, which lends credibility to the reliability of our measurement data. Figure 3 shows the temperature dependencies of the static dielectric constant $\epsilon(0)$. Each curve follows a Curie-Weiss type of law: $\epsilon(0) \equiv 1 + A_n/T$, with $A_n$ being an alcohol-specific variable explained further below. Note that $\epsilon(0)$ has the same nature as the main Debye relaxation $R_1$, because the latter gives 95% of the contribution to $\epsilon(0)$: the amplitude and position of the main relaxation $R_1$ determine the dielectric constant.

Discussion. As we experimentally observe uniform polarization dynamics of alcohols, we can unravel its underpinning physical mechanism. Accounting for quantum effects in liquids may be of importance to explain some of their properties [48-50]. Because water and alcohols share some common properties, we assume that proton intermolecular tunneling, a process well-identified in water [40, 51], also occurs in alcohols.

Figure 4 is a depiction of our alcohol model. Fig. 4a represents the double-well potential formed by two bounded molecules. The gray tails represent H(CH$_2$)$_n$ alkyl groups (for alcohols) or just one hydrogen atom H (for water). Each proton of the OH group has a non-zero probability to tunnel through the potential barrier. Such hydrogen bridges, where a proton with electric charge $q$, is delocalized between the molecules, continuously form and break on the subpicosecond timescale [53]. Note that the relaxation time $\tau_r$ (Table I) is larger. Proton tunneling requires two oxygen atoms to align exactly along the proton transfer line, which occurs on the 1-2 ps time scale [54]. When the bond breaks, the proton can detach from the parent molecule, and forms a proton-hole pair, or two ionic species, RO$^-$ and ROH$^+$ [55]. The energy difference between molecular and ionic states results from collective molecular effects in the adiabatic regime [56].

| $n$ | 1   | 2   | 3   | 4   | 10  |
|-----|-----|-----|-----|-----|-----|
| $D$ (nm$^2$·ns$^{-1}$) | 2.44 | 1.16 | 0.60 | 0.50 | 0.12 |
| $E$ (eV) | 0.13(3) | 0.20(1) | 0.24(1) | 0.25(1) | 0.26(1) |
| $\sigma_{dc}(0)$ (S·m$^{-1}$) | 6500 | 45100 | 32200 | 96300 | 2510 |
| $E_{dc}$ (eV) | 0.12(2) | 0.18(2) | 0.20(3) | 0.24(2) | 0.25(3) |
| $\sigma_{\infty}(0)$ (S·m$^{-1}$) | 4.77 | 1.22 | 0.41 | 0.24 | 0.027 |
| $E_{dc}$ (eV) | 0.13(2) | 0.20(2) | 0.23(2) | 0.25(2) | 0.27 |

Fig. 2. Normalized $\epsilon''/\epsilon''_{max}$ spectra of monohydric alcohols. Dashed line corresponds to the Debye relaxation model. Colored areas represent different regimes of the spectra: main relaxation (blue), its high frequency satellite (yellow), and the static conductivity (pink). The pink line is computed from our model and shows very good agreement with experimental data (circles) and some discrepancy with decanol only, but within the error bars.

Fig. 3. Temperature dependencies of (a) high-frequency conductivity, $\sigma_\infty$; (b) low-frequency static conductivity, $\sigma_{dc}$; and (c) dielectric constant, $\epsilon(0)$. Color lines are fit according to Arrhenius law and Curie-Weiss law. Parameters are in Table II. Numbers near curves are alcohols’ ordinal numbers. Figures shown are activation energies in eV.
The majority of newly-formed ions recombine within 1 ps \[57\]. Some of them, however, can live much longer. This lifetime is expected to be higher in alcohols because the probability of proton transfer is lower due to the increase in the degree of ionization; \(N_i\) and \(N_{dc}\) are molar concentrations of alcohol molecules, short- and long-lived proton-hole pairs; \(\alpha = N_i/(N_i + N_m)\) is the degree of ionization; \(pK_a\) and \(pK_a^{(model)}\) are dissociation constants \[52\], and those calculated in our study, respectively.

| \(d\) (nm) | 1    | 2    | 3    | 4    | 10   |
|------------|------|------|------|------|------|
| \(L\) (nm) |      |      |      |      |      |
| \(\tau_{OH}\) (ps) | 51   | 140  | 320  | 342  | 3207 |
| \(N_m\) (M)  | 24.7 | 17.2 | 13.3 | 10.9 | 5.25 |
| \(N_i\) (M)  | 0.5  | 0.3  | 0.2  | 0.1  | 0.05 |
| \(N_{dc} \times 10^6\) (M) | 6.2  | 8.5  | 5.3  | 3.9  | 0.32 |
| \(\alpha\) | 0.020| 0.017| 0.015| 0.010| 0.009|
| \(pK_a^{(model)}\) | 15.8 | 15.4 | 15.7 | 15.9 | 16.1 |
| \(pK_a\) | 15.5 | 15.5 | 16.1 | 16.1 |      |

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\[
s(\nu) = \frac{\sigma_{dc} + (2\pi\nu)^2\tau_1^2\sigma_{\infty}}{1 + (2\pi\nu)^2\tau_2^2}
\]

where \(\sigma_{dc} = q^2N_{dc}D/k_B T\), \(\sigma_{\infty} = q^2N_iD/k_B T\). We assume here the same frequency-independent diffusion coefficient \(D\) for excess protons and molecules (Table III), because an excess proton is always attached to one or another molecule.

Equation (1) reproduces well the experimental spectra of alcohols up to 0.1 THz (see Figs. 1 and 4d). For \(\nu \to \infty\) it gives the \(\sigma_{\infty}\) plateau, and for \(\nu \to 0\) the \(\sigma_{dc}\) plateau. These two plateaus correspond to the same mechanism of proton-hole separation, with equal activation energies \(E\), but the respective conductivity levels are different because if \(t < \tau_1\) all pairs contribute; if \(t > \tau_1\) only the long-lived pairs contribute. Comparing Eq. (1) with the experimental spectrum in Fig. 1, we find that \(\tau_1\) (main Debye relaxation \(R_1\)) coincides with \(\tau_1\) (proton-hole pairs lifetime). The ac-dc transition time equals \(\tau_2 = \tau_1\sqrt{\sigma_{\infty}/\sigma_{dc}}\). The model (1) assumes that the polarization in alcohols is due to translational diffusion of unbound charges, namely excess protons and proton holes with lifetimes determined by separation and recombination. The proton-hole dynamical structure is similar to a plasma in the frame of reference of the globally neutral molecular network.

Figure 4 illustrates our proposed mechanism. Yellow lines show excess protons trajectories (“wires”). A spontaneous relative displacement of charges (protons and holes) changes the dipole moment \(M(t) = q\Delta r(t)\) (black arrows) and its projection \(M_x(t) = q\Delta x(t)\) on the \(x\)-axis along the external electric field \(E\). Note that the position of the proton hole is shown fixed for simplicity. The corresponding polarization \(P_z(t) = (q \sum M_x(t))/V\) determines the dielectric function \(\epsilon(\nu) = 1 + P_z(\nu)/\epsilon_0 E\) and the dynamical conductivity \(\sigma(\nu) = 2\pi\nu\epsilon(\nu)\epsilon_0\). The lifetime distribution (Fig. 4b) imposes the wire length \(l(t) = \sqrt{2Dt}\). The unit-length segment \(l = d\) corresponds to \(l = \tau_{OH}\), and is equal to the distance \(d = 0.5 \times (3/(4\pi N_m))^{1/3}\) between OH groups of randomly oriented molecules (Table III). The time \(\tau_{OH}\) coincides with \(\tau_1\). The second length \(L\) represents the minimum length of proton wire required for the short-circuit (see ‘\(s/c\)’ in Fig. 4b), or dc conduction \(\sigma_{dc}\). The corresponding time \(t = \tau_2\), represents the moment when the mean-square-displacement spheres of protons start to overlap. The concentration \(N_{dc}\) of ionic species with lifetime \(\tau_2\) equals \(N_{dc} = 3/(4\pi L^3)\), and corresponds to the dissociation constant \(pK_a\) (Table II). Note that the percolation threshold does not depend on the sample thickness \[55\].

We can now derive the equation for the static dielectric constant, which according to the Debye formula reads: 

\[
\sigma(\nu) = \frac{\sigma_{dc} + (2\pi\nu)^2\tau_1^2\sigma_{\infty}}{1 + (2\pi\nu)^2\tau_2^2}
\]
\[ \epsilon(0) = \epsilon_{\text{THz}} + \sigma^\infty \tau_i / \epsilon_0, \]
from which we get:
\[ \epsilon(0) = \epsilon_{\text{THz}} + \frac{\epsilon^2 N_m^{1/2}}{k_B T \epsilon_0} \left( \frac{9}{2 \pi^2 K_a^{1/2}} \right)^{1/3} \]  \hspace{1cm} (2)

where \( \epsilon_{\text{THz}} \) is shown in Fig. 1a, and \( K_a = N_d^2 / N_m \) is the dissociation constant (Table III). Note that the molecular concentration \( N_m \) represents here the concentration of OH groups. Equation (2) fits well the experimental data including temperature dependencies (see lines in Fig. 3c). In contrast to the formula of the Debye-Onsager-Fröhlich-Kirkwood approach [29–31], Eq. (2) includes only one material-specific parameter, the dissociation constant \( K_a \), and does not require the knowledge the single-molecule dipole moment \( \mu \). Therefore, within our model, the proton-hole dipole moments are responsible for polarization in alcohols.

Note that our model gives a relatively high instantaneous concentration \( N_i \) of excess protons (\( \alpha \lesssim 2\% \) - see Table III). Our model does not contradict the \( pK_a \) because only a small part of \( N_i \) contribute to the static conductivity, while \( N_e \) contributes fully to the high-frequency dielectric response. We associate the \( O_1 \) band (Fig. 1c) to the excess proton oscillation in the double-well potential. Indeed, the oscillator frequency \( \nu = (2 \pi x)^{-1} \sqrt{2 \Delta E / m_p} \approx 2.5 \text{ THz} \), where \( m_p \) is the proton mass, \( x \approx 0.2 \text{ nm} \) is average O–O distance, and \( \Delta E \approx 0.2 \text{ eV} \) is the energy barrier [59], is close to \( \nu_0 \). Moreover, the lifetime of the excess proton state (the half-width of the \( \nu_0 \) band) is equal to 0.5 ps, which is close to the known lifetime of the transition state of proton between molecules [60, 61]. In light of our analysis, the mobile excess proton states of high concentration \( N_i \) but short lifetime, cause the local heterogeneity of alcohols, detected experimentally [62, 63], and provoke the concomitant rearrangement of the chain structures observed in [64].

Conclusion We experimentally measured the ultra-broadband dielectric response of five monohydric alcohols, and processed the data with a consistent methodology. We found similarities across the various alcohols, unexplained by existing polarization models. Introducing excess protons and holes with exponential lifetime distributions, we propose a non-rotational polarization mechanism, which accounts on the same footing for static (dc conductivity and dielectric constant) and dynamic (dielectric relaxation and high frequency conductivity) effects as microscopically connected phenomena. Our model permits a consistent spectral data analysis across alcohols and provides a physical explanation to support observed data.

The Authors acknowledge support of the Skoltech NGP Program (Skoltech-MIT joint project). E.C. also acknowledges the Skoltech Global Campus Program.

SUPPLEMENTAL MATERIAL

Samples preparation

For our experiments we used five primary alcohols listed in Table S1. All samples were purchased from the same manufacturer (Sigma-Aldrich), except ethanol (Fisher Chemical), and used as received. We used the samples with the highest available purity, i.e. 99.9%, except for decanol with only 98% purity, which explains the dispersion of data in Table S1. We used the samples with the highest available purity (see Table S1). All samples were purchased from the same manufacturer (Sigma-Aldrich), except ethanol (Fisher Chemical), and used as received. We used the samples with the highest available purity, i.e. 99.9%, except for decanol with only 98% purity, which explains the dispersion of data in Table S1.

Measurement procedure

The low- (megahertz), and high-frequency (gigahertz) measurements were performed using different sample holders and measuring cells. Alcohols were placed into measurement cells using Finnpipette renewed after each usage. The cell was washed with ethanol before each measurement and stored in a liquid to be measured for 5 minutes, heated up to 40°C. The dc measurements cell was thermally stabilized using acetone as a thermal conductive liquid, Peltier cooler for temperature control, and Pt1000 thermocouples for accurate temperature measurements. For the gigahertz region measurements, we used a copper bath, in which the sample in the glass beaker was tightly inserted. The open-end coaxial probe was applied at the liquid-air interface. At low frequencies, we used a cylindrical Teflon cell with two round-flat gold electrodes of 1 cm² each and separation about 1 mm. The complex impedance was measured.

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TABLE S1. List of alcohols used in this study in comparison with those from previous research.

| Alcohol     | This work        | Ref. [46] | Ref. [47] |
|-------------|------------------|-----------|-----------|
| Methanol    | Sigma-Aldrich, 99.9% | Fluka, 99.8% | Panreac, 99.8% |
| Ethanol     | Fisher Chemical, 99.9% | Fluka, 99.8% | Fluka, 99.8% |
| 1-Propanol  | Sigma-Aldrich, 99.9% | Fluka, 99.5% | Fluka, 99.5% |
| 1-Butanol   | Sigma-Aldrich, 99.9% | Fluka, 99.5% | Fluka, 99.5% |
| 1-Decanol   | Sigma-Aldrich, 98%  | -         | -         |

by the four-electrode method [41], as each alcohol was passing through the space between the electrodes at a constant flow rate controlled by the peristaltic pump.

The measuring rms voltage $V_{\text{rms}} = 100 \text{ mV}$ and signal intensity 45 dB were chosen well below the electrolysis stability threshold, 1.23 V, and such that the sample temperature and chemical composition remain stable. The low- and high-frequency measurements show comparable data for the static dielectric constant, and also for the static conductivity, which confirms the validity of our experimental approach. The real, $\epsilon'$, and imaginary, $\epsilon''$, parts of the complex dielectric permittivity are calculated from the measured complex impedance $Z^* = Z' + Z''$ with:

$$
\epsilon' = \frac{1}{C_0} \left( -\frac{Z''}{Z'^2 + Z''^2} \right) \omega
$$

$$
\epsilon'' = \frac{1}{C_0} \left( \frac{Z'}{Z'^2 + Z''^2} \right) \omega
$$

where $C_0$ is the capacitance of the empty cell. The dynamical conductivity is then obtained with its definition: $\sigma(\omega) = \epsilon''(\omega) \epsilon_0 \omega$.

**Self-diffusion and dielectric relaxation**

The self-diffusion coefficient of molecules in liquids can be measured independently by two main methods, which give similar results: isotopic substitution, and spin-echo NMR. The data on self diffusion of oxygen, and hydrogen atoms in alcohols, obtained by these methods are available in Refs. [46, 47]. For our study, it is important to know the mean square displacement $x$ of atoms on the timescale of the dielectric relaxation time $\tau_r$, which can be obtained using the self-diffusion coefficients $D$ calculated with the Smoluchowski formula $x = (6D \tau_r)^{1/2}$. Values are given in Table S2 for all alcohols considered in our work. As the molecular diffusion in liquids demonstrates hoping-like behavior [65], it would be informative to compare $x$ with the distance $d$ between centers of molecules. As one can see from Table S2, $x > d$; hence, over the relaxation time $\tau_r$, each molecule covers at least one intermolecular distance as it moves, or, in other words, changes its local environment. This means that inasmuch as dielectric relaxation in associated liquids (including alcohols) is a collective phenomenon, no cluster-like structures made of several molecules can explain the dielectric relaxation, as they simply cannot last sufficiently long for such a relatively long time as $\tau_r$.

**TABLE S2. Self-diffusion and dielectric relaxation parameters of primary alcohols.**

| n | 1 | 2 | 3 | 4 | 10 |
|---|---|---|---|---|----|
| $\tau_r$ (ps) | 54 | 177 | 370 | 549 | 1989 |
| $D$ (nm$^2$·ns$^{-1}$) | 2.44 | 1.16 | 0.60 | 0.50 | 0.12 |
| $x$ (nm) | 0.88 | 1.11 | 1.16 | 1.28 | 1.21 |
| $d$ (nm) | 0.50 | 0.57 | 0.62 | 0.66 | 0.84 |

[1] S. Mashimo, T. Umehara, Structures of water and pri-
mary alcohol studied by microwave dielectric analyses, J. Chem. Phys. 95, 6257 (1991).

[2] L. M. Wang, R. Richert, Dynamics of glass-forming liquids. IX. Structural versus dielectric relaxation in monohydroxy alcohols, J. Chem. Phys. 121, 11170 (2004).

[3] C. Gainaru, R. Meier, S. Schildmann, C. Lederle, W. Hiller, E. Rössler, and R. Böhmer, Nuclear-magnetic-resonance measurements reveal the origin of the Debye process in monohydroxy alcohols, Phys. Rev. Lett. 105, 258303 (2010).

[4] C. J. Clarke, W.-C. Tu, O. Levers, A. Bröhl and J. P. Hallett, Green and sustainable solvents in chemical processes, Chem. Rev. 118, 747 (2018).

[5] G. Merle, M. Wessling, K. Nijmeijer, Anion exchange membranes for alkaline fuel cells: A review, J. Membrane Sci. 377, 1 (2011).

[6] H. J. Edenberg, The genetics of alcohol metabolism: Role of alcohol dehydrogenase and aldehyde dehydrogenase variants, Alcohol Research & Health 30, 5 (2007).

[7] M. Tomsič, A. Jammik, G. Fritz-Popovski, O. Glatter, L. Vlček, Structural properties of pure simple alcohols from ethanol, propanol, butanol, pentanol, to hexanol: Comparing Monte Carlo simulations with experimental SAXS data, J. Phys. Chem. B 111, 1738 (2007).

[8] E. Carignani, C. Forte, E. Juszynska-Galazka, M. Galazka, M. Massalska-Arodź, M. Geppi, L. Calucci, Dynamics of two glass forming monohydroxy alcohols by field cycling 1H NMR relaxometry, J. Mol. Liq. 269, 847 (2018).

[9] M. Gasteiger, J. Behler, and P. Marquetand, Machine learning molecular dynamics for the simulation of infrared spectra, Chem. Sci. 8, 6924 (2017).

[10] T. Joo, Y. Jia, J.-Y. Yu, M. J. Lang, and G. R. Fleming, Third-order nonlinear time domain probes of solvation dynamics, J. Chem. Phys. 104, 6089 (1996).

[11] J. R. Partington, R. F. Hudson, K. W. Bagnall, Self-diffusion of aliphatic alcohols, Nature 169, 583 (1952).

[12] P. Sillrén, A. Matic, M. Karlsson, M. Koza, et al., Liquid 1-propanol studied by neutron scattering, near-infrared, and dielectric spectroscopy, J. Chem. Phys. 140, 124501 (2014).

[13] J. S. Hansen, A. Kisliuk, A. P. Sokolov, C. Gainaru, Identification of structural relaxation in the dielectric response of water, Phys. Rev. Lett., 116, 237601 (2016).

[14] L. Wang, R. Richert, Debye type dielectric relaxation and the glass transition of alcohols, J. Phys. Chem. B 109, 22, 11091 (2005).

[15] E. Gerstner, Liquids in no man’s land, Nature Phys. 8, 252 (2012).

[16] P. Lunkenheimer, S. Emmert, R. Gulich, M. Khler, M. Wolf, M. Schwab, and A. Loidl, Electromagnetic-radiation absorption by water, Phys. Rev. E 96, 062607 (2017).

[17] V. G. Artemov, E. Uykur, P. Kapralov, A. Kiselev, K. Stevenson, H. Ouerdane, and M. Dressel, Anomalously high proton conduction of interfacial water, J. Phys. Chem. Lett. 11, 3623 (2020).

[18] R. Böhmer, C. Gainaru, R. Richert, Structure and dynamics of monohydroxy alcohols: Milestones towards their microscopic understanding, 100 years after Debye, Physics Reports, 545, 125 (2014).

[19] G. B. Dutt, S. Doraiswamy, N. Periasamy, and B. Venkataraman, Rotational reorientation dynamics of polar dye molecular probes by picosecond laser spectroscopic technique, J. Chem. Phys. 93, 8498 (1990).

[20] H. Weingärtner, H. Nadolny, A. Olenikova, and R. Ludwig, Collective contributions to the dielectric relaxation of hydrogen-bonded liquids, J. Chem. Phys. 120, 11692 (2004).

[21] P. Debye, Theorie der Dipolmomente der Molekeln, Physik. Z. 13, 97 (1912).

[22] P. Debye, Polar Molecules (New York: Chemical Catalog Co., Inc., 1929).

[23] P. Debye, Dielektrische sättigung und behinderung der freien rotation in flüssigkeiten, Phys. Z. 36, 193 (1935).

[24] K. S. Cole and R. H. Cole, Dispersion and absorption in dielectrics I. Alternating current characteristics, J. Chem. Phys. 9, 341 (1941).

[25] K. S. Cole and R. H. Cole, Dispersion and absorption in dielectrics II. Direct current characteristics, J. Chem. Phys. 9, 98 (1942).

[26] J. B. Miles, The dielectric constant and electric moment of some alcohol vapors, Phys. Rev. 34, 964 (1929).

[27] W. J. Dannhauser, Dielectric study of intermolecular association in isometric octyl alcohols, Chem. Phys. 48, 1911 (1968).

[28] See Supplemental material for details.

[29] L. Onsager, Electric moments of molecules in liquids, J. Am. Chem. Soc. 58, 1486 (1936).

[30] J. G. Kirkwood, The Dielectric Polarization of Polar Liquids, J. Chem. Phys. 7, 911 (1939).

[31] H. Fröhlich, Theory of Dielectrics (Oxford University Press: London, 1949).

[32] S. H. Glarum, Dielectric theory of polar liquids, J. Chem. Phys. 33, 1371 (1960).

[33] R. H. Cole, Correlation theory of dielectric relaxation, J. Chem. Phys. 42, 637 (1965).

[34] P. H. Fang, Cole-Cole diagram and the distribution of relaxation times, J. Chem. Phys. 42, 3411 (1965).

[35] T. Gaudin, and H. Ma, A molecular contact theory for simulating polarization: application to dielectric constant prediction, PCCP 21, 14846 (2019).

[36] M. H. Jensen, C. Gainaru, C. Alba-Simionesco, T. Hecksher and K. Niss, Slow rheological mode in glycerol and glycerolwater mixtures, PCCP 20, 1716 (2018).

[37] T. Yamaguchi, M. Saito, K. Yoshida, T. Yamaguchi, Y. Yoda, M. Seto, Structural relaxation and viscoelasticity of a higher alcohol with mesoscopic structure, J. Phys. Chem. Lett. 9, 298 (2018).

[38] B. Maribo-Mogensen, G.M. Kontogeorgis, and K. Thomsen, Modeling of dielectric properties of complex fluids with an equation of state, J. Phys. Chem. B 117, 3389 (2013).

[39] C. A. Angell, K. L. Ngai, G. B. McKenna, P. F. McMullan, and S. W. Martin, Relaxation in glass-forming liquids II. Direct current characteristics, J. Phys. Chem. 95, 6257 (1991).

[40] X. Meng, J. Guo, J. Peng, J. et al., Direct visualization of concerted proton tunnelling in a water nanocluster, Nature Phys. 11, 235 (2015).

[41] F. Klemen, A. Schönhals, Eds., Broadband Dielectric Spectroscopy (Springer, Berlin, 2003).

[42] Y. Yomogida, Y. Sato, R. Nozaki, T. Mishina, J. Nakahara, Dielectric study of normal alcohols with THz timedomain spectroscopy, J. Mol. Liq. 154, 31 (2010).

[43] S. Sarkar, D. Saha, S. Banerjee, A. Mukherjee, P. Mandal, Broadband terahertz dielectric spectroscopy of alcohols, Chem. Phys. Lett. 678, 65 (2017).
[44] K. C. Pratt, W. Wakeham, Self-Diffusion in Water and Monohydric Alcohols, J. Chem. Soc., Faraday Trans. 2 73, 997 (1977).
[45] I. D. Robb, Ed., Microemulsions (Plenum: New York, 1982).
[46] M. Prego, O. Cabeza, E. Carballo, C. F. Franjo, and E. Jiménez, Measurement and interpretation of the electrical conductivity of 1-alcohols from 273 K to 333 K, J. Molec. Liq. 89, 233 (2000).
[47] M. Prego, E. Rilo, E. Carballo, C. Franjo, E. Jiménez, O. Cabeza, Electrical conductivity data of alkanols from 273 to 333 K, J. Molec. Liq. 102, 83 (2003).
[48] T. F. Miller III and D. E. Manolopoulos, Quantum diffusion in liquid water from ring polymer molecular dynamics, J. Chem. Phys. 123, 154504 (2005).
[49] S. Habershon, T. E. Markland, and D. E. Manolopoulos, Competing quantum effects in the dynamics of a flexible water model, J. Chem. Phys. 131, 024501 (2009).
[50] V. N. Novikov, A. P. Sokolov, Role of quantum effects in the glass transition, Phys. Rev. Lett. 110, 065701 (2013).
[51] V. G. Artemov, E. Uykur, S. Roh, A. Pronin, H. Ouerdane, and M. Dressel, Revealing excess protons in the infrared spectrum of liquid water, Scientific Reports, in press (2020) - [arXiv:1910.07578]
[52] I. Ugur, A. Marion, S. Paradot, J. H. Jensen, G. Monard, Rationalization of the pKa values of alcohols and thiols using atomic charge descriptors and its application to the prediction of amino acid pKa’s, J. Chem. Inform. and Modeling 54, 2200 (2014).
[53] K. Mazur, M. Bonn, J. Hunger, Hydrogen bond dynamics in primary alcohols: A femtosecond infrared study, J. Phys. Chem. B 119, 1558 (2015).
[54] O. Markovitch, H. Chen, S. Izvekov, F. Paesani, G. A. Voth, N. Agmon, Special pair dance and partner selection: Elementary steps in proton transport in liquid water, J. Phys. Chem. B 112, 9456 (2008).
[55] A. Pietropaolo, R. Senesi, C. Andreani, A. Botti, M. A. Ricci, F. Bruni, Excess of proton mean kinetic energy in supercooled water, Phys. Rev. Lett. 100, 127802 (2008).
[56] L. Lin, J.A. Morone, R. Car, M. Parrinello, Displaced path integral formulation for the momentum distribution of quantum particles, Phys. Rev. Lett. 105, 110602 (2010).
[57] A. Hassanali, F. Giberti, J. Cuny, T.D. Kühne, M. Parrinello, Proton transfer through the water gossamer, PNAS 110, 13723-13728 (2013).
[58] I. Balberg, N. Binenbaum, N. Wagner, Percollation thresholds in the three-dimensional sticks system, Phys. Rev. Lett. 52, 1465 (1984).
[59] I. Sedov, B. Solomonov, Gibbs free energy of hydrogen bonding of aliphatic alcohols with liquid water at 298 K, Fluid Phase Equilibria 315, 16 (2012).
[60] M. Thämer, L. De Marco, K. Ramassesha, A. Mandal and A. Tokmakoff, Ultrafast 2D IR spectroscopy of the excess proton in liquid water, Science 350, 78 (2015).
[61] C. Gainaru, S. Kastner, F. Mayr, P. Lunkenheimer, S. Schildmann, H.J. Weber, W. Hiller, A. Loidl, R. Böhmer, Hydrogen-bond equilibria and lifetimes in a monohydry alcohol, Phys. Rev. Lett., 107, 118304 (2011).
[62] J.-H. Guo, Y. Luo, A. Augustsson, S. Kashtanov, J.-E. Rubensson, D. K. Shuh, H. gren, J. Nordgren, Molecular structure of alcohol-water mixtures, Phys. Rev. Lett., 91, 157401 (2003).
[63] J. Gabriel, F. Pabst, A. Helbling, T. Böhmer, T. Blochowicz, Nature of the Debye process in monohydroxy alcohols: 5-methyl-2-hexanol investigated by depolarized light scattering and dielectric spectroscopy, Phys. Rev. Lett., 121, 035501 (2018).
[64] L.P. Singh, R. Richert, Watching hydrogen-bonded structures in an alcohol convert from rings to chains, Phys. Rev. Lett., 109, 167802 (2012).
[65] J. Frenkel, Kinetic theory of liquids (Clarendon Press, Oxford, 1946).