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Picosecond Dynamics and Microheterogenity of Water + Dioxane Mixtures

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Dielectric spectra from 200 MHz up to 3 THz were determined to study the fast dynamics of dilute water + 1,4-dioxane. $\hat{\epsilon}(\nu)$ could be fitted by a collision induced oscillator at high frequencies plus two Debye relaxations in the microwave region. Isotope substitution was used to assign water and dioxane modes. The presence of the cooperative hydrogen-bond network relaxation down to a water mole fraction of 0.005 suggests a microheterogeneous structure of the mixtures even at low water content. The collision mode of dioxane at ~2 THz grows upon water addition, revealing the presence of H_2O molecules in dioxane-rich domains.

Introduction

Fast cooperative dynamics in water and other strongly associated hydrogen-bonding (H-bonding) liquids is not only of fundamental importance for aqueous chemistry but also of major interest in protein research and biology,[1] with many implications for living organisms as well as for artificial nanostructured systems.[2,3] Although H-bond dynamics in neat water and near hydrophobic molecules is reasonably well understood,[3−7] the molecular picture of cooperativity and microheterogeneity in mixtures remains limited,[8] especially at the rather low free water concentrations found in moderately polar (e.g., biological) environments. The dielectric relaxation of liquids in the high gigahertz to terahertz (far-infrared, FIR) range of the electromagnetic spectrum is particularly useful for probing dipolar entities, be it individual molecules or clusters.[9−11] However, due to the experimental difficulties associated with spectroscopy in this region, most studies suffer from insufficient frequency coverage, which is crucial for a detailed analysis of the spectra.[11] Recent technological advances[12] and improvement of existing methods make this field now more accessible.[7] By combination of frequency-domain reflectometry (FDR), travelling-wave interferometry (IF), and terahertz time-domain spectroscopy (THz-TDS) we obtained data over virtually the entire dielectric spectrum, $\hat{\epsilon}(\nu) = \epsilon'(\nu) - i\epsilon''(\nu)$ (frequency ν, permittivity ϵ', dielectric loss ϵ''), relevant for intermolecular interactions. Dioxane (DX) + water was selected as a model system because DX is fully miscible with water despite negligible polarity (static relative permittivity $\epsilon = \lim_{\nu\to 0} \epsilon' = 2.2095$). Dioxane may act as an H-bond acceptor but does not form aggregates with other dioxane molecules due to lacking H-bond donor sites.

Experimental Methods

1,4-Dioxane (DX, Merck, Germany; analytical grade, 99.97 mol %) for the preparation of the mixtures was distilled after drying with calcium hydride, yielding H_2O traces <30 ppm. For measurements with pure DX, UV spectroscopic grade material (Fluka, Switzerland) was extensively dried (<15 ppm H_2O) and then distilled and handled under dry N_2. Perdeuterated 1,4-Dioxane-d_8 (DX-d_8, Cambridge Isotope Laboratories, USA; isotope enrichment 99.2%) was dried over activated 4 Å molecular sieves. High-purity water (Millipore Milli-Q system) was used throughout. Deuterium oxide (Euriso-top, France; isotope enrichment ≥99.9%) was used as received. Mixtures were prepared gravimetrically without buoyancy correction and checked by Karl Fischer titration. Concentrations were expressed as mass fraction of water, w_1, and as mole fraction of dioxane (2) H-bond acceptor sites, $x_{0,2} = 2x_2/(1 + x_2)$.

All spectra were recorded at 25 ± 0.1 °C. FDR measurements (0.2−20 GHz) were performed with a Hewlett-Packard (HP) model 85070M dielectric probe system and corrected for calibration errors by the method described elsewhere.[13] IF data were obtained with two waveguide interferometers ($27 \leq \nu/\text{GHz} \leq 39$ and $60 \leq \nu/\text{GHz} \leq 89$)[14] and supplemented by literature data.[15] The terahertz setup covering 0.3−3 THz[16,17] was equipped with a Teflon-windowed cell where the sample path length was set to 1.5 or 2.3 mm by spacers made of gold plated, hardened steel. To account for drift, each sample measurement was bracketed by two reference measurements with dry nitrogen from which the actual path length was obtained to ±1μm using the reflections at the gas/window interfaces.

Results and Discussion

Neat Dioxane. The dielectric spectra of DX and DX-d_8 (Figure 1) were determined with THz-TDS and IF experiments in the frequency range $60 \leq \nu/\text{GHz} \leq 3000$. For DX the power absorption coefficient, α, shows a maximum at 1.98 THz (Figure 1b) and $\epsilon''(\nu)$ peaks at ~1.5 THz (Figure 1c). Additionally, a minimum is observed for $\epsilon'(\nu)$ (not shown) as well as for the

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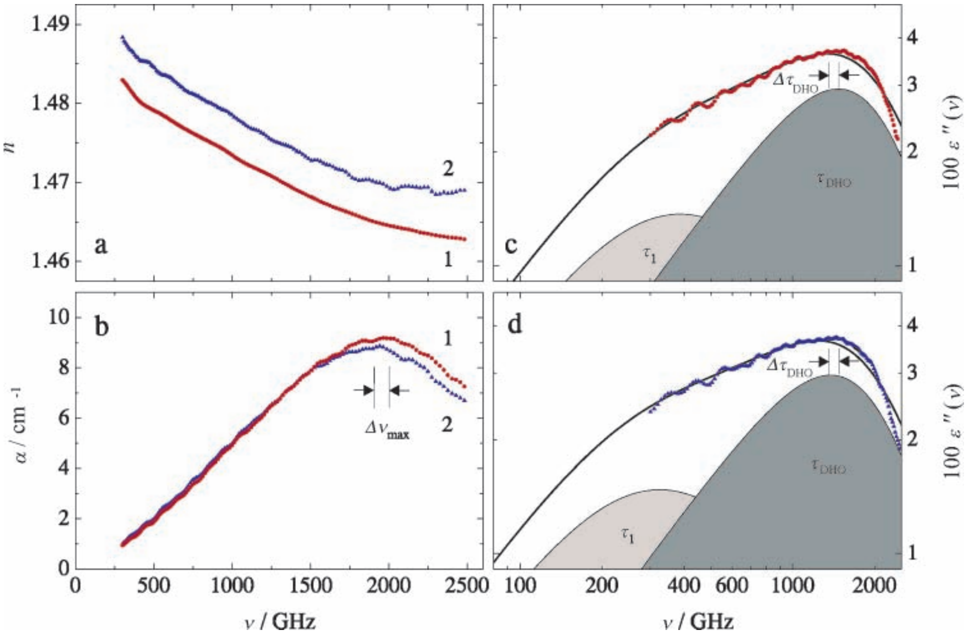

Figure 1. Terahertz refractive index (a) and absorption coefficient (b) of dioxane (1) and dioxane-d_8 (2) at 298 K. (c) and (d) compare the experimental dielectric loss (symbols) of dioxane (c) and dioxane-d_8 (d) with the fit, eq 1. Shaded areas indicate the contributions of the Debye (τ_1) and the DHO term (τ_{DHO}). The isotope shift in the peak frequencies of α and the DHO term is indicated.

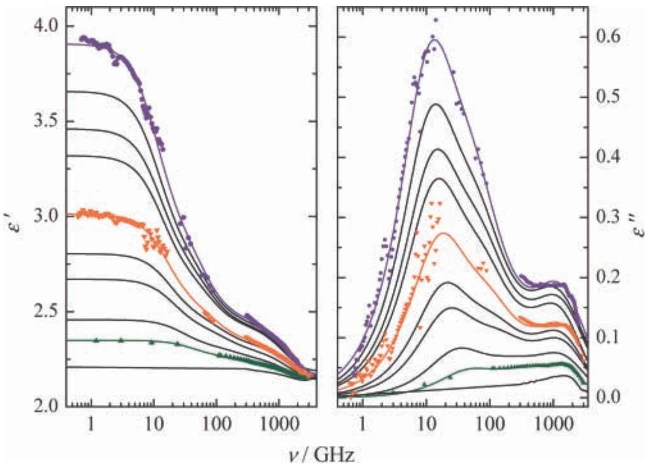

Figure 2. Fit curves (lines) of dielectric permittivity (a) and loss (b) spectra of water + dioxane mixtures at 298 K and water mass fractions $w_1 = 0$, 0.0051, 0.0089, 0.0161, 0.0203, 0.0249, 0.0355, 0.0395, 0.0448, and 0.0486 (bottom to top). For representational clarity experimental data (symbols) are only shown for full-range spectra ($w_1 = 0.0051$, 0.0249, and 0.0486).

refractive index, n, at ~2.6THz (Figure 1a, see also Figure 5b). These results agree with an early Fourier transform interferometry study of liquid DX in the FIR by Davies et al.[18] who concluded from the band shape that this mode is intermolecular (the lowest intramolecular vibration is at ~230 cm^{-1} [19]) and of resonance origin, arising from collision-induced dipoles. This terahertz absorption is similar in peak frequency but not in band shape to the unassigned low-frequency Raman band of DX.[20]

To a first approximation, the collision frequency of molecules in a liquid is proportional to their mean molecular velocity, υ, determined by thermal energy and molecular mass, m. This should be especially true for molecules that differ only in isotopic composition. Because $\upsilon^2 \sim (3k_BT)/(2m)$, the maximum of the dielectric loss of DX-d_8 should be shifted to lower frequencies by a factor of $r = \sqrt{m_{d_8}/m_{h_8}} = 0.957$ compared with that of DX. From the experimental $\epsilon''(\nu)$ (Figure 1c,d) a ratio of the peak frequencies of $r_{obs}(\epsilon'') = 0.95 \pm 0.01$ was obtained by graphical evaluation. The peak frequencies of the power absorption coefficient (Figure 1b; $\nu_{\max,h_8} = 1.98$ THz, $\nu_{\max,d_8} = 1.90$ THz), yielded an isotope effect of $r_{obs}(\alpha) = 0.96 \pm 0.01$, whereas for the damped harmonic oscillator mode (DHO) fitted to the high-frequency part of $\epsilon''(\nu)$ (see below, marked τ_{DHO} in Figure 1c,d) $r_{obs}(\text{DHO}) = 0.94$ is obtained. Our experimental results are in excellent agreement with the isotope effect predicted for intermolecular collisions and thus confirm the previous assignment[18] of the 2 THz mode of DX to an intermolecular vibration.

The dielectric spectra of pure DX and DX-d_8 are best fitted by the sum of a low-frequency Debye equation and a damped harmonic oscillator term (DHO), eq 1. The DHO contribution,

$$\hat{\epsilon}(\omega) = \epsilon_\infty + \frac{\epsilon_1 - \epsilon_2}{1 + i\omega\tau_1} + \frac{(\epsilon_2 - \epsilon_\infty){\omega_0}^2}{({\omega_0}^2 - \omega^2) + i\omega{\tau_{DHO}}^{-1}} \qquad \omega = 2\pi\nu \quad (1)$$

describing the intermolecular vibrations at ~2 THz, dominates $\hat{\epsilon}(\nu)$. However, a small-amplitude contribution (for both, DX and DX-d_8: $S_1 = \epsilon_1 - \epsilon_2 \approx 0.03$; $\tau_1 = 0.5^{+0.5}_{-0.2}$ ps) at low frequencies is evident from the experimental data. Dioxane is a flexible molecule with several conformers but NMR studies[21] and calculations[22] suggest that in the liquid at ambient temperatures the interconversion between the nonpolar chair and the two dipolar boat conformers is slow. Thus, it is reasonable to assign the slow relaxation to the rotational diffusion of a small amount of dipolar conformers, like the boat or twisted boat (both having $\mu \approx 2$D[23]), present in liquid DX besides the dominating nonpolar chair conformer. The relaxation time of such polar conformers is difficult to predict because they are nearly spherical and thus have small friction coefficients for rotation[24] but comparison with similar molecules suggests a value of 1−5 ps.[25] Keeping in mind the roughness of this estimation and the limited low-frequency coverage of $\hat{\epsilon}(\nu)$ the agreement with the experimental τ_1 is fair enough to support our assignment. In any case, the small magnitude of S_1 and the absence of any other dielectric relaxation at lower frequencies indicate that the fraction of dipolar DX conformers is $\lesssim$1% and thus the average

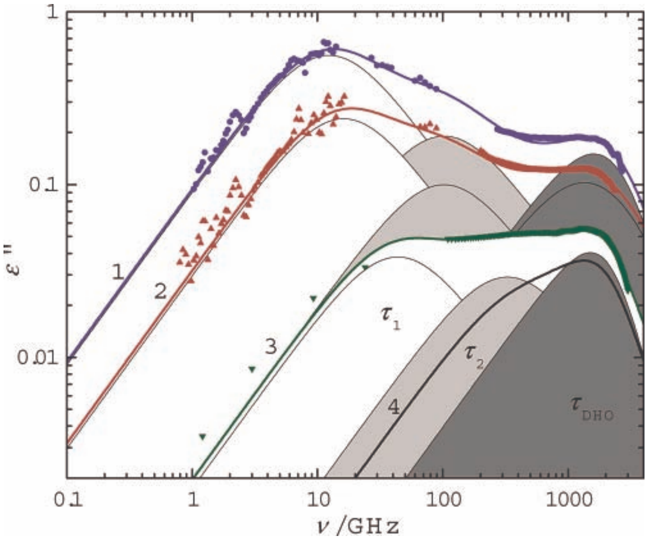

Figure 3. Experimental dielectric loss spectra (symbols) and fits (lines) of water + dioxane mixtures at $w_1 = 0.0486$ (1), 0.0249 (2), 0.0051 (3), and 0 (4, fit only). The shaded areas show the contributions of the cooperative water relaxation (τ_1), the secondary relaxation (τ_2) and the damped harmonic oscillator mode (τ_{DHO}) of dioxane.

dipole moment of DX molecules in the liquid $\bar{\mu} = 0.06 \pm 0.1$ D. Larger values occasionally given in the literature (e.g., 0.45 D[26]) result from neglecting the DHO mode in the THz region and erroneously ascribing the entire difference between static permittivity and the square of the refractive index at optical frequencies to the rotational diffusion of permanent dipoles. Our findings also resolve the disagreement among recent ab initio calculations regarding the importance of dipolar conformers in liquid DX.[27,28]

Dilute Solutions of Water in 1,4-Dioxane. The admixture of water to neat DX causes a large increase of the absorption coefficient. This reduces the bandwidth of the THz spectrometer to 0.3−2 THz for the highest water content of this study and prevents measurements at water mass fractions $w_1 > 0.05$. For three samples, $x_{\mathrm{O},2} = 0.89$, 0.94, and 0.99 (corresponding to $w_1 = 0.0486$, 0.0249, and 0.0051), $\hat{\epsilon}(\nu)$ was determined over the entire frequency range of $0.2 \leq \nu/\mathrm{GHz} \leq 2000{-}3000$, whereas for the remaining samples of Figure 2 only terahertz spectra were recorded. The full-range spectra were fitted by a combination of two Debye equations and a DHO term (i.e., eq 1 with an additional Debye term; see Figure 3) with the static permittivity, ϵ, fixed to interpolated literature data.[29] The fit parameters τ_1, ϵ_2, τ_2, and ϵ_3 were found to be smooth functions of the mole fraction $x_{\mathrm{O},2}$ (Figure 4). This allowed interpolation of ϵ, τ_1, ϵ_2, and τ_2 to the concentrations of the remaining samples and to fit their $\hat{\epsilon}(\nu)$ with only ϵ_3, τ_{D}, ω_0, and ϵ_∞ adjustable. Figure 4 shows that the obtained parameters are of good quality.

Dielectric relaxation studies over the entire DX-water composition range[29] show that the low-frequency Debye mode (relaxation time $\tau_1 = 8.4$ ps for neat H_2O[7]) can be assigned to the cooperative relaxation of the hydrogen-bond network of water. Its amplitude, S_1, increases rapidly with rising water content, Figure 4a. According to molecular dynamics simulations this relaxation is caused by water aggregates comprising 10−40 molecules.[30,31] Addition of a component like dioxane, which may act as an H-bond acceptor but not as a donor, should have large effects on the H-bond network relaxation by modifying the size distribution and environment of the water clusters. Indeed, already at the dilute water solution of $x_{\mathrm{O},2} = 0.95$, where 95 out of 100 hydrogen-bond acceptor sites beong to dioxane molecules, τ_1 is longer than in pure water (Figure 4b).

Strong water−dioxane interactions, invoking even the formation of more or less stable hydrates, were often held responsible for the peculiar thermodynamic properties of DX−water mixtures. However, the water−ether oxygen hydrogen bond is weak compared with the water−water H-bond.[32] Therefore, the large local energy fluctuations in liquid water of up to 60 kJ/mol (ca. 5 times the H-bond strength)[30,31] are in variance with the assumption of stable DX−H_2O aggregates in aqueous mixtures. The large amplitude S_1, as well as the long τ_1 suggest that the cooperative H-bond mode is preserved even at our lowest water concentration, $w_1 = 0.005$, possibly by the formation of water clusters which are stiffened due to the reduced number of accessible H-bond configurations compared

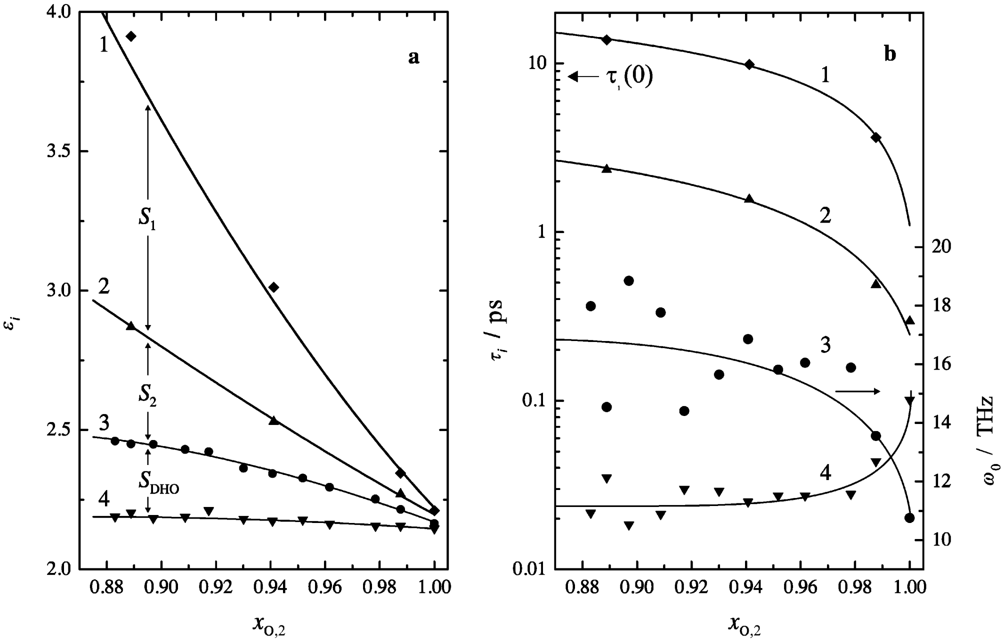

Figure 4. (a) Limiting permittivites (ϵ (1), ϵ_2 (2), ϵ_3 (3), ϵ_∞ (4)) and (b) characteristic times (τ_1 (1), τ_2 (2), τ_{DHO} (4)), respectively, and DHO shape parameters (ω_0 (3)) of water + dioxane mixtures at 298 K as a function of the dioxane-specific H-bond acceptor mole fraction, $x_{\mathrm{O},2}$. Lines for τ_{DHO} and ω_0 are only guide to the eye.

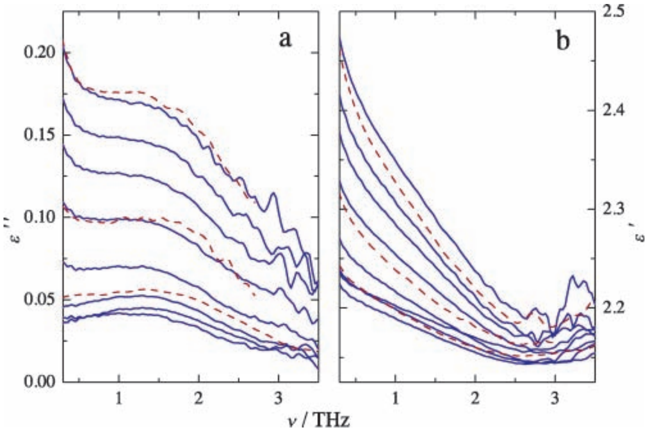

Figure 5. Spectra of dielectric loss (a) and permittivity (b) of D_2O + dioxane at 298 K and D_2O weight fractions $w_1 = 0$, 0.0028, 0.0042, 0.0097, 0.0196, 0.0301, 0.0397, 0.0496 (solid line, bottom to top). Broken lines are H_2O + dioxane at $w_1 = 0.0051$, 0.0161, and 0.0448.

to pure water. Recent molecular dynamics studies of closely related water + polyethylene oxide systems[33,34] also suggest the presence of sizable water aggregates even at a large excess of acceptor sites (ether groups). We cannot confirm previous dielectric relaxation studies below 10 GHz[35] and low-frequency Raman data[20] claiming a breakdown of the water clusters already at $x_{O,2} \approx 0.33$. It seems that the interpretations given in these papers are marred because either the study does not cover the relevant frequency range[35] or had insufficient signal-to-noise ratio to resolve the small water contribution at $x_{O,2} > 0.85$.[20] But note that in agreement with our results the *B* band at ∼1.5 THz, assigned by Tominaga and Takeuchi[20] to a bending-like mode among water molecules, remains detectable down to their lowest water concentration.

The relaxation time of the intermediate Debye process (τ_2 in Figure 3) decreases from 3 ps at $x_{O,2} = 0.89$ to 0.5 ps for pure dioxane (Figure 4b). Its amplitude, S_2, strongly increases with the water content (Figure 4a). The magnitudes of S_2 and τ_2 exclude an identification of this mode with the fast relaxation of pure water at ∼ 0.4 ps.[7] Supported by the NMR results of Takamuku et al.[36] we suggest that this process—in addition to a small contribution from the few DX molecules with polar conformations (see above)—mainly arises from the relaxation of H_2O molecules that are not incorporated in the tetrahedral H-bond network of the prevailing water clusters but reside within dioxane-rich regions. Such water molecules are either free or form weak hydrogen bonds with the oxygen sites of DX. However, the exchange of H_2O molecules between H-bonding clusters and the monomer state must be rapid. Otherwise macroscopic phase separation would occur. The addition of water also leads to an appreciable increase of ϵ'' in the terahertz region (Figure 2) reflected in the increased amplitude of the DHO mode, S_{DHO} (Figure 4a). Within experimental error the shape of the resonant contribution (expressed by ω_0) and the peak position (τ_{DHO}) remain almost unchanged (Figure 4b). Also, the shape of the THz spectra does not change when H_2O is replaced by D_2O, Figure 5. This clearly indicates that the rapid increase of S_{DHO} with increasing water content is directly connected with the DHO mode of DX. Because this band essentially arises from fluctuations of the induced dipole moment that is generated by colliding DX molecules these must be strongly polarized by the presence of H_2O dipoles.

The presented data show that the DHO mode of DX acts as a probe for the presence of water molecules. From the values of τ_{DHO} and ω_0 (Figure 4b) it can be concluded that already for water contents as low as $w_1 \approx 0.009$ ($x_{O,2} \approx 0.98$) all dioxane molecules experience the presence of H_2O dipoles. Simultaneously, the cooperative relaxation of water-rich domains also already appears at this surprisingly low w_1.

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