Thermal Decoupling of Molecular-Relaxation Processes from the Vibrational Density of States at Terahertz Frequencies in Supercooled Hydrogen-Bonded Liquids

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ABSTRACT: At terahertz frequencies, the libration-vibration motions couple to the dielectric relaxations in disordered hydrogen-bonded solids. The interplay between these processes is still poorly understood, in particular at temperatures below the glass transition temperature, T_g, yet this behavior is of vital importance for the molecular mobility of such materials to remain in the amorphous phase. A series of polyhydric alcohols were studied at temperatures between 80 and 310 K in the frequency range of 0.2−3 THz using terahertz time-domain spectroscopy. Three universal features were observed in the dielectric losses, $\epsilon''(\nu)$: (a) At temperatures well below the glass transition, $\epsilon''(\nu)$ comprises a temperature-independent microscopic peak, which persists into the liquid phase and which is identified as being due to librational/torsional modes. For $0.65\,T_g < T < T_g$, additional thermally dependent contributions are observed, and we found strong evidence for its relation to the Johari−Goldstein secondary β-relaxation process. (b) Clear spectroscopic evidence is found for a secondary β glass transition at $0.65\,T_g$, which is not related to the fragility of the glasses. (c) At temperatures above T_g, the losses become dominated by primary α-relaxation processes. Our results show that the thermal changes in the losses seem to be underpinned by a universal change in the hydrogen bonding structure of the samples.

SECTION: Glasses, Colloids, Polymers, and Soft Matter
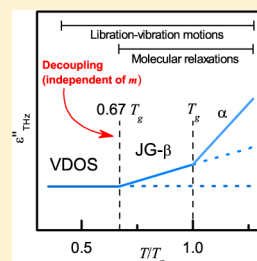
Glass-forming liquids have intriguing physical properties that have long been the subject of intense research, both experimentally and theoretically.[1] The molecular dynamics probed by electromagnetic fields, which conventionally have been observed by light scattering and dielectric and infrared (IR) spectroscopy, often show a strikingly similar response for a wide range of disordered systems.[2] The interaction of far-IR radiation with supercooled liquids is commonly described in terms of the vibrational density of states (VDOS) that forms the libration-vibration band, also called the microscopic peak, in the region ∼1−5 THz.[3−6] At lower frequencies, the existence of a primary (α) and a secondary (β) relaxation process,[7] as well as the existence of a fast-β relaxation that is predicted by mode-coupling theory (MCT),[8,9] can be resolved using dielectric-spectroscopy and light-scattering measurements. Although the interplay between the different relaxation processes has been studied in some detail,[10] there is little understanding of the relationship between these relaxation processes and the microscopic peak.

In this Letter, we investigate, using terahertz time-domain spectroscopy (THz-TDS), the origin of the experimentally observed dielectric losses, in the frequency range 0.2−3 THz and the temperature range 80−310 K (straddling the glass-transition temperature), using a series of intermolecular hydrogen-bonded polyalcohols, $C_n(OH)_nH_{n+2}$: glycerol ($n = 3$), threitol (4), xylitol (5), and sorbitol (6). These glass-forming liquids show a systematic change in the fragility index, $m = \partial(\log \eta)/\partial(T_g/T)_{T=T_g}$, that is, in the degree of the non-

Arrhenius temperature dependence of the viscosity, η, $m = 57$ (glycerol), 79 (threitol), 94 (xylitol), 128 (sorbitol),[11] indicative of a decreasing extent of a hydrogen-bonded network. Moreover, these materials show significant differences in their dielectric spectra. They can be ordered in terms of the observation of Johari−Goldstein β (JG-β) relaxation, from a wing-type scenario to a fully resolved JG-β relaxation peak, in the series glycerol, threitol, xylitol, and sorbitol.[11] Both well below and well above T_g, only limited experimental dielectric-loss spectra are available at near-terahertz frequencies in the literature for these and other glass-formers obtained by conventional methods.[12,13] Our THz-TDS data show a universal response among the studied polyalcohol samples for the microscopic peak at terahertz frequencies, and the first observation of the JG-β relaxation vanishing from terahertz spectra universally at the temperature $0.6\,T_g$.

THz-TDS has previously been used to investigate the dynamics of disordered materials, such as monohydric alcohols[14,15] as well as glycerol[16] and sorbitol (and its aqueous solutions).[17] However, a systematic THz-TDS study, over a wide temperature range, of the polyalcohols has not previously been performed. This technique allows direct access to the

complex dielectric function for the frequency range of 0.2−3 THz, over a broad temperature range.

THz-TDS directly measures both the absorption coefficient α and refractive index n of materials. These properties can then be used to calculate the real ϵ' and imaginary ϵ'' part of the dielectric losses as

$$\epsilon'(\nu) = n(\nu)^2 - \kappa(\nu)^2$$

$$\epsilon''(\nu) = 2n(\nu)\kappa(\nu) = \frac{2n(\nu)\alpha(\nu)c}{4\pi\nu} \qquad (1)$$

where c is speed of light in vacuum, κ is the extinction coefficient and ν is linear frequency. It was determined that the absorption coefficient suffers from a frequency-independent background of roughly 5 cm^{-1} that needs to be subtracted from the absorption spectra in order to match the dielectric losses obtained by high-frequency dielectric spectroscopy[12,18] and THz-TDS. The inaccuracy in α further limits the resolution of THz-TDS. For a given thickness of the sample, the absorption coefficient is measured with an accuracy of $\Delta\alpha \sim 1-2$ cm^{-1} over the covered frequency range. Given eq 1, this causes a higher uncertainty in dielectric losses $\Delta\epsilon''$ at lower terahertz frequencies: at 1 THz, $\Delta\epsilon'' \sim 0.015$; at 0.5 THz, $\Delta\epsilon'' \sim 0.03$. In particular, this causes the low-frequency, low-temperature resolution cutoff in terahertz dielectric losses as seen in Figure 1.
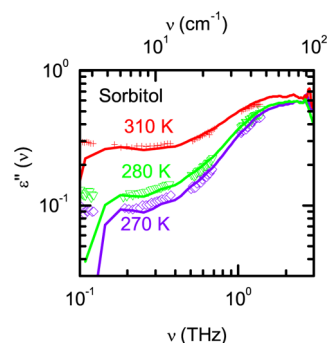

Figure 1. Comparison of dielectric losses $\epsilon''(\nu)$ at terahertz frequencies as obtained by dielectric spectroscopy[12] (data points) and terahertz spectroscopy (solid lines) for sorbitol at 270−310 K.

The dielectric losses of the samples in the glassy state at the lowest temperatures are almost independent of temperature and comprise a microscopic peak at a frequency around 2−3 THz, as seen in Figure 2 and far-infrared spectra.[19] The peak is still evident for $T > T_g$, but the amplitude now increases with increasing temperature. We assert that the microscopic peak observed in the THz-TDS data in Figure 2 is a manifestation of a peak in the VDOS due to low-lying, optically active librational/torsional modes. Calculations of the internal vibrational modes in the isolated glycerol molecule show that the lowest (torsional) mode occurs at 2.01 THz.[20] Moreover, lattice-dynamics calculations of phonons in crystalline glycerol, used to generate the orientationally averaged (powder) glass-like dynamical structure factor in the incoherent approximation, indicate a peak at ∼1.5 THz.[20] The lowest-frequency optical modes in crystalline glycerol are observed from RS to occur at 1.65 THz. These findings support our assertion that the microscopic peak in Figure 2 is due to low-frequency librational/torsional modes in these materials.

As the samples are heated, a temperature-dependent contribution to the dielectric losses develops. This is mostly apparent for temperatures above T_g (red line in Figure 2), yet in the case of sorbitol, xylitol, and threitol, it may be observed also below T_g. The induced relative change in the losses is highest at the lowest frequencies and resemble the tail of a broad peak with a maximum at frequencies below the covered spectral window. This links the origin of this loss to the primary dielectric-relaxation process.[21] At T_g, the primary dielectric relaxation corresponds to relaxation times of around 100 s,[22] far too low to contribute to $\epsilon''(\nu)$ in the terahertz regime. Upon heating above T_g, the primary relaxation rapidly shifts to higher frequencies, resulting in the observed increase in dielectric losses. The decoupling of the primary dielectric relaxation from the temperature-independent microscopic peak may be related to the intermolecular bonding. It has been shown that in hydrogen-bonding systems, the nonbonded −OH groups become hydrogen-bonded during the glass transition.[23] Terahertz spectroscopy, thus, observes the glass transition on the intermolecular level, at least in the hydrogen-bonded systems, which is an intrinsic property of the material rather than a matter of convention (e.g., related to the viscosity reaching 10^{12} Pa·s).

The change in losses with temperature below T_g are roughly one order of magnitude weaker compared to the contribution of the α-relaxation to the dielectric losses above T_g. This suggests that the source of the losses below T_g no longer originates from the α-relaxation process. A change in ϵ'' of the order of 10^{-2} with a 10 K increment was observed at gigahertz frequencies in dielectric spectra of sorbitol below T_g and can be assigned to the JG-β relaxation.[24] Therefore, it is possible to
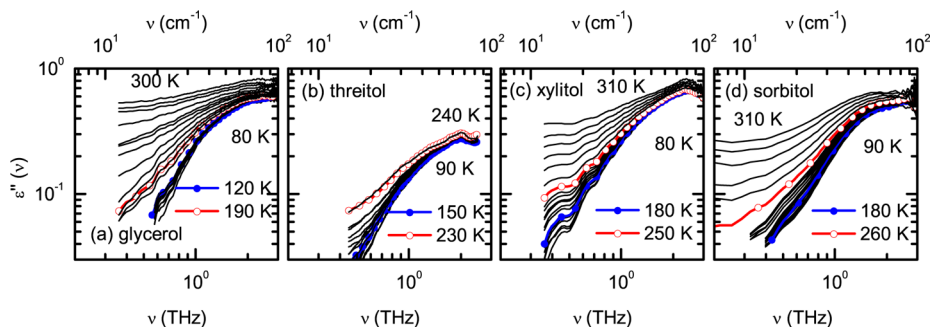

Figure 2. Dielectric losses $\epsilon''(\nu)$ of (a) glycerol, (b) threitol, (c) xylitol, and (d) sorbitol at terahertz frequencies 0.2−3 THz in the temperature range 80−310 K with 10 K temperature increments. The blue and red circles highlight the losses in the proximity of $0.65T_g$ and T_g, respectively. The sample of threitol recrystallized above 250 K; therefore, no data above this temperature are shown in this figure.

assign the thermally dependent changes in the spectra below T_g to the JG-β relaxation. This is examined further below.

In order to examine the thermal changes of the losses further, we plot the temperature dependence of $\epsilon''(\nu)$ at $\nu = 1$ THz for all studied samples as shown in Figure 3. We use the rescaled
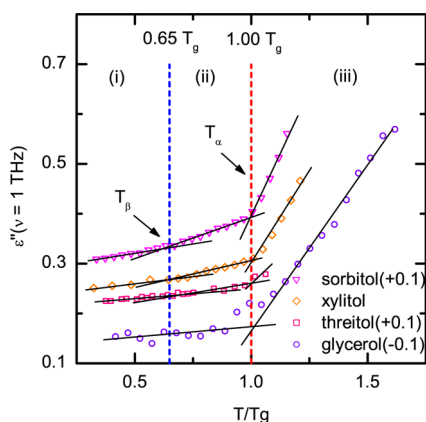

Figure 3. Dielectric losses $\epsilon''(T/T_g)$ at frequency $\nu = 1$ THz. The solid lines represent linear fits of regions (i), (ii), and (iii) as explained in the text. The dashed vertical blue and red lines highlight $0.65T_g$ and $1.00T_g$, respectively. T_β and T_α represent the crossing point of the linear fits from area (i) to area (ii) and from area (ii) to area (iii), respectively. The dielectric loss data for sorbitol, threitol, and glycerol are offset in the positive (+0.1) and negative (−0.1) direction for clarity.

temperature T/T_g on the abscissa to compare the common features of the glassy state between the different polyalcohols. Three absorption regimes can be resolved in general: (i) temperature-independent losses, (ii) a weak temperature dependence of losses below T_g, and (iii) a strong temperature dependence of losses above T_g, as proposed previously.[17] More detailed information was extracted by fitting the data points with an empirical linear fit, namely, $\epsilon''(T/T_g) = A + BT/T_g$, in the respective temperature regions. In Table 1, we summarize the crossover temperatures T_β and T_α between regions (i)–(ii) and (ii)–(iii), respectively, together with the respective gradients $B_{1,2,3}$ obtained separately for each region, (i), (ii) and (iii). For all samples, T_α corresponds to T_g, the temperature above which the temperature-dependent part of $\epsilon''(\nu)$ becomes dominated by the primary dielectric relaxation.

The plot reveals two striking features. First, it shows that the weak temperature dependence of losses (region (ii) in Figure 3) for threitol, xylitol, and sorbitol emerges at a temperature of around $0.65 T_g$ in all cases except glycerol. Considering the fact that the thermal changes of ϵ'' originate from the secondary relaxation, and most likely from the JG-β relaxation, this means that the secondary relaxation decouples completely from the

microscopic peak at around $0.65T_g$. This observation is in excellent qualitative agreement with calorimetric studies of glass-forming liquids, where the β-glass-transition temperature was linked to spontaneous temperature drift rates in the region of 0.6–$0.7T_g$.[26−28] Fujimori and Oguni[26] originally proposed a correlation between the fragility index m and a "correlation index" c, defined as $(1 - c) = T_{g\beta}/T_{g\alpha}$. From our study, however, it is apparent that such a correlation does not hold because these polyalcohols cover a range of different fragilities, yet in all cases, the onset of secondary relaxation is observed in the range of 0.6–$0.7T_g$. It should also be noted that the shift of the secondary relaxation to lower frequencies upon cooling below T_g is a well-known phenomenon from dielectric studies.[12,25,29] Commonly, T_g is associated with $\tau_\alpha = 100$ s.[22] A similar extrapolation of $\tau_\beta = 100$ s from the dielectric data for sorbitol[12,30] and xylitol[12] leads to $T_{g\beta} \approx 160 \pm 5$ K, for both sorbitol and xylitol, which is in good agreement with observed T_β values in Table 1. These results, together with the fact that no knee around $0.65T_g$ is observed in the case of glycerol, where only an excess wing to α-relaxation is normally present, strongly support the proposal that the observed temperature variation between $0.65T_g$ and T_g originates from the JG-β relaxation.

The second striking observation in the terahertz data is that the temperature gradient, B_2, of the dielectric losses in region (ii) varies significantly between the samples (see Table 1). Based on the value of B_2, the polyalcohols can be arranged in the series, glycerol, threitol, xylitol, and sorbitol, that is, in increasing order of fragility, in analogy with how well the JG-β relaxation peak is resolved from the primary relaxation in the dielectric spectrum at lower frequencies, from an excess wing in glycerol to the strong JG-β peak in sorbitol.[11] A previous study revealed that the number of −OH groups in polyhydric alcohols plays an essential role in the slow dynamics of these materials.[24] This hints that the hydrogen-bonding character of molecules in these glasses plays a similar role in both primary and secondary relaxation. One of the implications is that the observations presented in this Letter may be characteristic of hydrogen-bonded systems only, and hence, it is important to examine non-hydrogen-bonded systems in future.

In addition to the primary and secondary relaxation, a fast-β relaxation process that falls into the gigahertz−terahertz frequency range is predicted.[8,9] Most commonly, this fast-β relaxation has been explained in terms of a rattling movement of entire molecules in cages formed by the molecules in their immediate vicinity.[9] The contribution from the fast-β relaxation process to $\epsilon''(\nu)$ spectra has been confirmed experimentally above $T_c \approx 1.2T_g$ in dielectric spectroscopy of glycerol, xylitol, and sorbitol.[12,18] The predictions of MCT for temperatures below T_c are limited due to missing data covering the gigahertz−terahertz region at these temperatures,[31] and

Table 1. Glass-Transition Temperature, T_g, Together with the Linear-Fit Analysis of Dielectric Losses, $\epsilon''(T/T_g) = A + BT/T_g$, As Shown in Figure 3[a]

sample	n	$T_g(K)$[1]	$T_\alpha(K)$	$T_\beta(K)$	T_β/T_g	B_1	B_2	B_3
sorbitol	6	268.3	269	178	0.66	0.08 ± 0.01	0.18 ± 0.01	1.06 ± 0.06
xylitol	5	247.8	253	176	0.71	0.06 ± 0.01	0.12 ± 0.01	0.83 ± 0.04
threitol	4	226.3	216	146	0.64	0.04 ± 0.01	0.06 ± 0.01	0.25 ± 0.09
glycerol	3	191.7	194			0.00 ± 0.06	0.04 ± 0.04	0.67 ± 0.02

[a]n stands for the number of OH groups per molecule. T_β and T_α represent the crossover points of the linear fits from region (i) to region (ii) and from region (ii) to region (iii), respectively. $B_{1,2,3}$ are the linear coefficients obtained from fits in regions (i), (ii), and (iii), respectively.

deviations from MCT predictions immediately below T_c were shown by the dielectric studies.[12,18] Given the match between the dielectric data and THz-TDS data above T_g, it is clear that we observe similar effects that are commonly attributed to contributions to the losses originating from fast-β relaxation (Figure 2). Given the results of this Letter, this means that the frequency region of fast-β relaxation is directly influenced by both α and JG-β relaxations; this fact must be taken into account in future theoretical predictions. It is also necessary to extend the present study to temperatures well above $1.2T_g$ to elucidate further relationships between all three relaxations and the VDOS.

Lastly, from Figure 3 and Table 1, it is apparent that some small temperature changes in the spectra exist also at temperatures below $0.65T_g$. Two explanations are possible. First, this may be due to a different secondary relaxation, such as pseudo-JG secondary relaxation.[32] Second, although the microscopic peak is considered as a temperature-independent feature, given its vibrational origin, it may exhibit a slight red shift as well as broadening upon heating. The red shift and broadening of the terahertz absorption feature upon heating in low-viscous liquids, referred to as the Poley absorption peak, was reported previously.[33] To elucidate which mechanism is playing a role here, a further study covering the full microscopic peak in the full temperature range is necessary.

In conclusion, using terahertz time-domain spectroscopy, we have studied dielectric losses in the supercooled hydrogen-bonded polyalcohols, glycerol, threitol, xylitol, and sorbitol, at terahertz frequencies, at temperatures both above and below T_g. The results reveal several universal features among the samples. At the lowest temperatures, the losses comprise the microscopic peak due to librational/torsional modes. As the glasses are heated above $0.65T_g$, the dielectric losses increase steadily with temperature. There is strong evidence that this feature originates from the high-frequency tail of the JG-β relaxation. It is best observed in the case of sorbitol, whereas it remains unobservable in the case of glycerol. Temperatures in the proximity of $0.65T_g$ appear to be the universal region for the secondary glass transition due to the JG-β relaxation in several systems, but with no correlation to the fragility, as has been proposed previously.[26] When the glasses are heated above T_g, the dielectric losses become dominated by the high-frequency tail of the α-relaxation that shifts to higher frequencies. In the proximity of the glass transition, the primary dielectric relaxation decouples from the libration-vibration band. The decoupling seems to be related to the change in the hydrogen bonding of the glasses. The temperature variation of the losses, both above and below T_g, that originate from relaxation processes increases with the number of $-OH$ groups per molecule. This finding highlights the fact that the character of intermolecular bonding plays an important role in both primary and secondary relaxations. The results show that the gigahertz–terahertz frequency region is directly influenced by both α and JG-β relaxations and this fact must be taken into account in future theoretical predictions on fast-β relaxation below T_c. Further terahertz investigations of both hydrogen-bonded and non-hydrogen-bonded glasses are necessary in order to examine the universality of the decoupling of relaxation processes from the librational and vibrational modes, in particular with regards to the JG-β relaxation.

■ EXPERIMENTAL SECTION

All samples were melted (except glycerol, which is liquid at room temperature), and the molten liquid was loaded into a cuvette consisting of two round z-cut quartz windows of 13 mm diameter separated by a plastic ring spacer with a nominal thickness of either 190 or 450 μm. The cuvette was attached to a coldfinger of a continuous-flow cryostat and cooled at a rate of approximately 25 K min^{-1} to 80 K, followed by subsequent heating by 10 K increments to 310 K. Spectra were acquired using a custom-built THz-TDS setup operating in transmission geometry.[17] All materials were purchased from Sigma-Aldrich with purity >99% and used without further purification.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Biroli, G.; Garahan, J. P. Perspective: The Glass Transition. *J. Chem. Phys.* **2013**, *138*, 12A301.
(2) Lunkenheimer, P.; Loidl, A. Response of Disordered Matter to Electromagnetic Fields. *Phys. Rev. Lett.* **2003**, *91*, 207601.
(3) Strom, U.; Hendrickson, J. R.; Wagner, R. I.; Taylor, P. C. Disorder-Induced Far Infrared Absorption in Amorphous Materials. *Solid State Commun.* **1974**, *15*, 1871−1875.
(4) Strom, U.; Taylor, P. C. Temperature and Frequency Dependences of the Far-Infrared and Microwave Optical Absorption in Amorphous Materials. *Phys. Rev. B: Solid State* **1977**, *16*, 5512−5522.
(5) Möller, K. D.; Rothschild, W. G. *Far-infrared Spectroscopy*; Wiley: New York, 1971; p 794.
(6) Wong, J.; Angell, C. A. *Glass: Structure by Spectroscopy*; M. Dekker: New York, 1976.
(7) Johari, G. P.; Smyth, C. P. Dielectric Relaxation of Rigid Molecules in Supercooled Decalin. *J. Chem. Phys.* **1972**, *56*, 4411.
(8) Götze, W. Recent Tests of the Mode-Coupling Theory for Glassy Dynamics. *J. Phys.: Condens. Matter* **1999**, *11*, A1.
(9) Götze, W. *Complex Dynamics of Glass-Forming Liquids*; Oxford University Press: New York, 2009.
(10) Ngai, K. L. Relation Between some Secondary Relaxations and the α Relaxations in Glass-Forming Materials According to the Coupling Model. *J. Chem. Phys.* **1998**, *109*, 6982.
(11) Döß, A.; Paluch, M.; Sillescu, H.; Hinze, G. From Strong to Fragile Glass Formers: Secondary Relaxation in Polyalcohols. *Phys. Rev. Lett.* **2002**, *88*, 095701.
(12) Kastner, S.; Köhler, M.; Goncharov, Y.; Lunkenheimer, P.; Loidl, A. High-Frequency Dynamics of Type B Glass Formers Investigated by Broadband Dielectric Spectroscopy. *J. Non-Cryst. Solids* **2011**, *357*, 510−514.
(13) Lunkenheimer, P.; Loidl, A. High-Frequency Excitations in Glassy Crystals. *J. Non-Cryst. Solids* **2006**, *352*, 4556−4561.
(14) Yomogida, Y.; Sato, Y.; Yamakawa, K.; Nozaki, R.; Mishina, T.; Nakahara, J. Comparative Dielectric Study of Pentanol Isomers with Terahertz Time-Domain Spectroscopy. *J. Mol. Struct.* **2010**, *970*, 171−176.

(15) Yomogida, Y.; Sato, Y.; Nozaki, R.; Mishina, T. Comparative Dielectric Study of Monohydric Alcohols with Terahertz Time-Domain Spectroscopy. *J. Mol. Struct.* **2010**, *981*, 173−178.

(16) Miao, Q.; Tian, L.; Zhao, K.; Zhou, Q.; Shi, Y.; Zhao, D.; Zhao, S.; Zhang, C. Detection and Identification of Selected Alcohols Using Terahertz Time-domain Spectroscopy. *J. Phys. (Paris)* **2011**, 012220.

(17) Sibik, J.; Shalaev, E. Y.; Zeitler, J. A. Glassy Dynamics of Sorbitol Solutions at Terahertz Frequencies. *Phys. Chem. Chem. Phys.* **2013**, *15*, 11931−11942.

(18) Lunkenheimer, P.; Pimenov, A.; Dressel, M.; Goncharov, Y.; Böhmer, R.; Loidl, A. Fast Dynamics of Glass-Forming Glycerol Studied by Dielectric Spectroscopy. *Phys. Rev. Lett.* **1996**, *77*, 318−321.

(19) Sibik, J.; Zeitler, J. A. University of Cambridge, Cambridge, U. K. *Unpublished data*, 2014.

(20) Bermejo, F. J.; Criado, A.; de Andres, A.; Enciso, E.; Schober, H. Microscopic Dynamics of Glycerol in Its Crystalline and Glassy States. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1996**, *53*, 5259−5267.

(21) Lunkenheimer, P.; Kastner, S.; Köhler, M.; Loidl, A. Temperature Development of Glassy α-Relaxation Dynamics Determined by Broadband Dielectric Spectroscopy. *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.* **2010**, *81*, 051504.

(22) Angell, C. A.; Ngai, K. L.; McKenna, G. B.; McMillan, P. F.; Martin, S. W. Relaxation in Glassforming Liquids and Amorphous Solids. *J. Appl. Phys.* **2000**, *88*, 3113−3157.

(23) Barkatt, A.; Angell, C. A. Optical Probe Studies of Relaxation Processes in Viscous Liquids. *J. Chem. Phys.* **1979**, *70*, 901−911.

(24) Nakanishi, M.; Nozaki, R. High-Frequency Broadband Dielectric Spectroscopy on Sugar Alcohols below T_g. *J. Non-Cryst. Solids* **2010**, *356*, 733−737.

(25) Nakanishi, M.; Nozaki, R. Systematic Study of the Glass Transition in Polyhydric Alcohols. *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.* **2011**, *83*, 051503.

(26) Fujimori, H.; Oguni, M. Correlation Index $(T_{ga} - T_{gb})/T_{ga}$ and Activation Energy Ration as Parameters Characterizing the Structure of Liquid and Glass. *Solid State Commun.* **1995**, *94*, 157−162.

(27) Kishimoto, K.; Suga, H.; Seki, S. Calorimetric Study of the Glassy State. VIII. Heat Capacity and Relaxational Phenomena of Isopropylbenzene. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 3020−3031.

(28) Alba-Simionesco, C.; Fan, J.; Angell, C. A. Thermodynamic Aspects of the Glass Transition Phenomenon. II. Molecular Liquids with Variable Interactions. *J. Chem. Phys.* **1999**, *110*, 5262−5272.

(29) Kubo, E.; Minoguchi, A.; Sotokawa, H.; Nozaki, R. Nearly Constant Dielectric Loss of Polyhydric Alcohols. *J. Non-Cryst. Solids* **2006**, *352*, 4724−4728.

(30) Wagner, H.; Richert, R. Equilibrium and Non-Equilibrium Type beta-Relaxations: D-Sorbitol versus *o*-Terphenyl. *J. Phys. Chem. B* **1999**, *103*, 4071−4077.

(31) Gotze, W.; Sjogren, L. Relaxation Processes in Supercooled Liquids. *Rep. Prog. Phys.* **1992**, *55*, 241−376.

(32) Ngai, K. L.; Paluch, M. Classification of Secondary Relaxation in Glass-Formers Based on Dynamic Properties. *J. Chem. Phys.* **2004**, *120*, 857−73.

(33) Johari, G. P. Molecular Inertial Effects in Liquids: Poley Absorption, Collision-Induced Absorption, Low-Frequency Raman Spectrum and Boson Peaks. *J. Non-Cryst. Solids* **2002**, *307−310*, 114−127.

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