

ULTRA-SLOW RELAXATION DYNAMICS IN TRIGLYCINE SULFATE AND *D*-SORBITOL STUDIED BY TIME-RESOLVED SPECTROSCOPY

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Abstract

The ultra-slow modes with a relaxation time much longer than 1 ns are discovered by a time-resolved spectroscopy in uniaxial ferroelectric $(\text{NH}_2\text{CH}_2\text{COOH})_3\text{H}_2\text{SO}_4$ (TGS) and in glass-former $\text{HOCH}_2(\text{CHOH})_4\text{CH}_2\text{OH}$ (*D*-sorbitol). A mode discovered in TGS is a thermal relaxational mode and is proved to be the physical origin of the central peak found by Brillouin scattering. Two modes are discovered in *D*-sorbitol. One is a thermal relaxational mode. The other is a mode characterized by the Kohlraush-Williams-Watts function with a relaxation time τ_R . A remarkable result is that τ_R indicates a critical behavior not at the liquid-glass transition temperature $T_g = -7^\circ\text{C}$ but at the ergodic to nonergodic transition temperature $T_c = 33^\circ\text{C}$.

Keywords: *D*-sorbitol, time-resolved spectroscopy, triglycine sulfate

Introduction

Triglycine sulfate $(\text{NH}_2\text{CH}_2\text{COOH})_3\text{H}_2\text{SO}_4$ (TGS) is a typical uniaxial ferroelectric material undergoing the phase transition at about $T_c = 49^\circ\text{C}$. In the ferroelectric phase below T_c , the spontaneous electric polarization appears along the *b* axis. In this material, a central peak with zero frequency shift has been found by Brillouin scattering [1]. The peak intensity of the central peak shows remarkable anisotropic feature; a λ type anomaly presents along the *c* axis but no anomaly presents along the polar *b* axis. The line width of the central peak was too narrow to be analyzed by a usual Fabry-Perót interferometer (the spectral resolution limit of which is about 1 GHz). For this reason, two different interpretations about the physical origin of the central peak have been proposed; a thermal relaxational mode (fluctuation of temperature or entropy) [1] and a polarization relaxational mode (fluctuation of electric polarization) [2]. The direct measurement of the line width of the central peak, the inverse of which is a relaxation time of the mode, is essential for the mode identification. Therefore, an experimental technique having a spectral resolution limit much higher than 1 GHz is necessary to determine the origin. The time-resolved spectroscopy must be an attractive technique. If one uses a picosecond pulse laser, one can easily establish the time resolution of 1 ns. The time region longer

than 1 ns corresponds to the frequency region lower than 1 GHz, meaning that the time-resolved spectroscopy can realize the spectral resolution limit higher than 1 GHz.

D-sorbitol $\text{HOCH}_2(\text{CHOH})_4\text{CH}_2\text{OH}$ is a fragile glass-former with linear carbon-chains and hydrogen-bond networks. The liquid-glass transition temperature and melting point are $T_g = -7^\circ\text{C}$ and $T_m = 97^\circ\text{C}$, respectively [3]. The two-step relaxation of the density-fluctuation correlation function is predicted by the mode-coupling theory (MCT) [4]; a slow relaxation step is called the α relaxation and a fast one is called the β relaxation. The β relaxation has been studied by the combined system of Brillouin and Raman scattering apparatuses, and the ergodic to nonergodic transition predicted by MCT has been found to occur at $T_c = 33^\circ\text{C}$ [5]. Since the slow relaxation step is expected to be in the frequency region much lower than 1 GHz, it can not be investigated even by Brillouin scattering due to the spectral resolution limit of Fabry-Perot interferometer. The time-resolved spectroscopy is an attractive technique also in this case.

The purposes of this paper are to review the experimental data clarifying the physical origin of the central peak in TGS [6] and to report the dynamical behavior of the slow relaxation step newly found in *D*-sorbitol.

Experimental

Two TGS samples were prepared for the measurement of the modes propagating along the a^* , b and c axes. One was the b plate sample of size $5.4 \times 7.7 \times 0.6 \text{ mm}^3$ for the modes with the wave vector \mathbf{q} parallel to the a^* and c axes. The other was the c plate sample of size $2.5 \times 5.5 \times 0.8 \text{ mm}^3$ for the mode with \mathbf{q} parallel to the b axis. The ferroelectric transition temperature T_c was determined to be 48.5°C from the dielectric measurement. On the other hand, the *D*-sorbitol sample was prepared by melting the powder reagent purchased from Nacalai Tesque Ltd and by drying in vacuum at about 120°C for 24 h.

The time-resolved spectroscopy called impulsive stimulated thermal scattering (ISTS) is performed. In ISTS, a $\text{Nd}^+:\text{YLF}$ laser (Quantronix 4271) was used for the excitation of modes at the wavelength of $\lambda_E = 1053 \text{ nm}$. A single pulse of 110 mJ and 60 ps emitted from the laser was split into two pulses. These two pulses were polarized vertically and crossed inside the sample with a crossing angle of θ_E . A spatially coherent mode (fluctuation of density) was excited impulsively with $|\mathbf{q}| = (2\pi/\lambda_E)2\sin(\theta_E/2)$. The density fluctuation arises from the thermal expansion associated with the pulse energy absorption into O-H and/or C-H vibration overtones. In order to probe the excited mode, the vertically polarized probe beam from cw Ar^+ gas laser (Spectra-Physics BeamLok 2060) with $\lambda_P = 514.5 \text{ nm}$ was focused on the excitation area with Bragg angle θ_B so as to be diffracted by the excited mode. The angle θ_B was calculated from the formula; $\lambda_P/\sin(\theta_B/2) = \lambda_E/\sin(\theta_E/2)$. The Bragg-diffracted probe beam was detected by a photomultiplier tube (Hamamatsu R1636) and was stored as a real time signal intensity $I(t)$ in a digitizing oscilloscope (Tektronix TDS744A) after being accumulated 10,000 times.

Results and discussion

TGS

We review here the results obtained in TGS by the ISTS experiment [6]. The ultra-slow relaxational modes were discovered with the wave vectors $\mathbf{q} // a^*$, b and c axes. The value of $|\mathbf{q}|$ was $7.5 \times 10^3 \text{ cm}^{-1}$, because θ_E was set to be 7.2° . The time dependence of the mode intensity $I(t)$ observed at $T=44.6^\circ\text{C}$ is plotted in Fig. 1 on a semi-logarithmic scale. The intensity $I(t)$ clearly shows a simple exponential decay with a single relaxation time τ of about $10 \mu\text{s}$ in order. The diffusion constant $D=1/(\tau|\mathbf{q}|^2)$ calculated from the values of τ and $|\mathbf{q}|$ is plotted in Fig. 2. Since the dif-

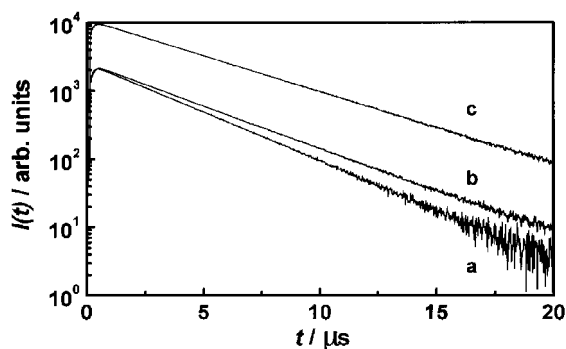


Fig. 1 The real time signal intensity $I(t)$ caused by the relaxational mode with $|\mathbf{q}|=7.5 \times 10^3 \text{ cm}^{-1}$ at $T=44.6^\circ\text{C}$. a – $\mathbf{q} // a^*$, b – $\mathbf{q} // b$ and c – $\mathbf{q} // c$ axes [6]

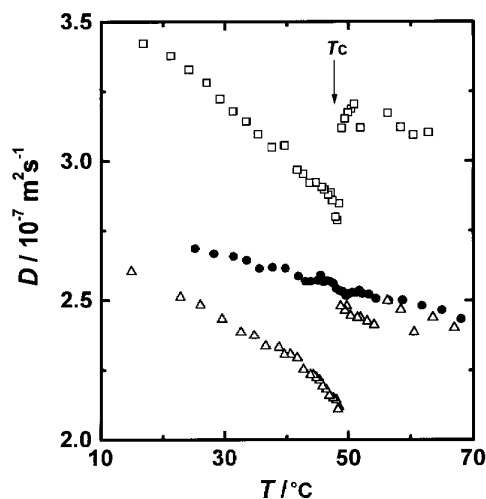


Fig. 2 The temperature dependence of the diffusion constant $D=1/(\tau|\mathbf{q}|^2)$ of the relaxational mode with $|\mathbf{q}|=7.5 \times 10^3 \text{ cm}^{-1}$; $\mathbf{q} // a^*$ (squares), $\mathbf{q} // b$ (closed circles) and $\mathbf{q} // c$ (triangles) axes [6]

fusion constant was found to be almost the same as the thermal diffusivity D_{th} measured by heat pulse method [7], the discovered mode was identified to be a thermal relaxational mode. The temperature and \mathbf{q} -direction dependences of the intensity at time origin $I(0)$ are plotted in Fig. 3 with open circles. The theoretical formulation of $I(0)$ for a thermal relaxational mode has been already obtained as [8, 9]

$$I(0) \propto (\alpha/C_X)^2 \quad (1)$$

Here α is the thermal expansion coefficient and C_X is the specific heat at constant stress X . The value of $(\alpha/C_X)^2$ was evaluated from the reported values of α and C_X [10–12] and was plotted in Fig. 3 by a curved full line.

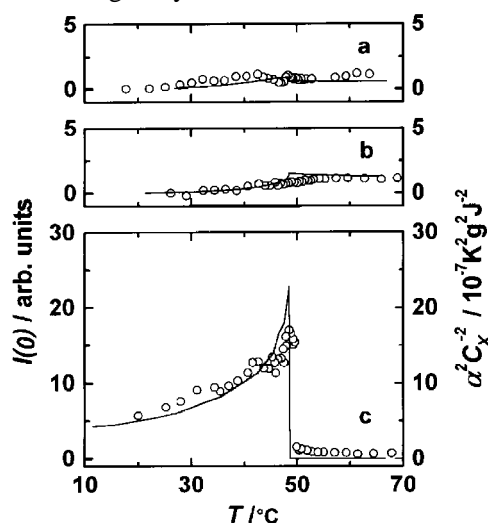


Fig. 3 The temperature dependence of the real time signal intensity at time origin $I(0)$ caused by the thermal relaxational mode (circles) and the temperature dependence of the calculated value of $(\alpha/C_X)^2$ (curved full lines); a – $\mathbf{q} // a^*$, b – $\mathbf{q} // b$ and c – $\mathbf{q} // c$ axes [6]

The coincidence between the observed data and the line was excellent. It should be mentioned here that the temperature and \mathbf{q} -direction dependences of $I(0)$ were explained mainly by those of α . The temperature and \mathbf{q} -direction dependences of $I(0)$ were quite similar to those of Landau-Placzek ratio $R_{LP} = I_R / (2I_B)$ obtained by Brillouin scattering [1]; a λ type anomaly presents along the c axis but no anomaly presents along the polar b axis. Here I_R and I_B are the integrated intensity of the central peak and that of the Brillouin peak, respectively. The similarity between $I(0)$ and R_{LP} strongly implied that the physical origin of the central peak discovered by Brillouin scattering is the thermal relaxational mode found in the present experiment. The authors evaluated R_{LP} as

$$R_{LP} \propto (\alpha^2 T c_s) / (\rho C_X) \quad (2)$$

where c_S is the elastic stiffness constant at constant entropy S and ρ is the density of the sample. It was found from this equation that the temperature and \mathbf{q} -direction dependences of R_{LP} are determined mainly by those of α . As both of $I(0)$ and R_{LP} were found to be characterized mainly by α , their similarity is a matter of course. This finding led the conclusion that the physical origin of the central peak in TGS must be the thermal relaxational mode observed in the present ISTS experiment.

The authors discussed the other interpretation that a polarization relaxational mode is the physical origin of the central peak [2]. The relaxation time of the polarization fluctuation has been determined by Brillouin scattering to be about 4×10^{-11} s at $T_c - T = 1^\circ\text{C}$ [13]. If the polarization relaxational mode is the origin, the spectral width of the central peak should be about 10 GHz. However, the width observed in Brillouin scattering was around 1 GHz [1], indicating that the physical origin is not the polarization relaxational mode.

D-sorbitol

Figure 4 shows a typical temperature dependence of the observed mode intensity $I(t)$. The value of $|\mathbf{q}|$ was $1.3 \cdot 10^4 \text{ cm}^{-1}$ at $\theta_E = 12.5^\circ$. Two modes are found in $I(t)$. One is a thermal relaxational mode existing mainly at the time region longer than the time t_m when $I(t)$ takes a maximum value. It can be seen from Fig. 4 that t_m is about $1 \mu\text{s}$ at $T = 36^\circ\text{C}$. The other mode is a new one existing mainly in the time region shorter than t_m . This type of the mode is usually assigned to a structural relaxation (α relaxation) in glass-formers; glycerol, triphenylphosphite, salol and so on [14]. But the mode discovered in the present study is different from the α relaxation as shown later. When the relaxation process of the new mode is assumed to be described by the

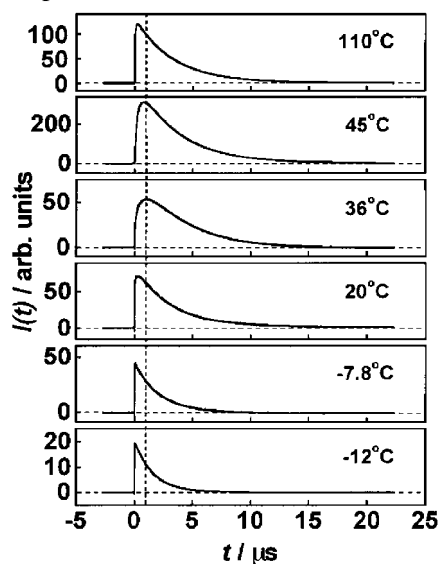


Fig. 4 Typical temperature dependence of the signal intensity $I(t)$

Kohlraush-Williams-Watts stretched exponential function $\exp[-(t/\tau_R)^\beta]$ with a relaxation time τ_R and a stretching constant β , $I(t)$ is expressed by a following equation [15]

$$I(t) = \{A\exp(-t/\tau_H) - B\exp[-(t/\tau_R)^\beta]\}^2 \quad (3)$$

Here A and B are coefficients dependent on temperature, and the first term represents the thermal relaxational mode with a relaxation time τ_H . The obtained $I(t)$ can be fitted successfully to this equation. With the decrease of the temperature, the value of β decreases from 1.0 ± 0.1 at $T=110^\circ\text{C}$ and takes the minimum value of 0.3 ± 0.2 at around $T=33^\circ\text{C}$, and increases to 1.0 ± 0.1 at $T=-10^\circ\text{C}$. The temperature dependences of τ_H and τ_R are plotted in Figs 5 and 6, respectively. Especially, the temperature dependence of τ_R is remarkable. The relaxation time τ_R seems to show a critical behavior (a tendency of divergence) not at the liquid-glass transition temperature $T_g=-7^\circ\text{C}$ but at the ergodic to nonergodic transition temperature $T_c=33^\circ\text{C}$. The temperature

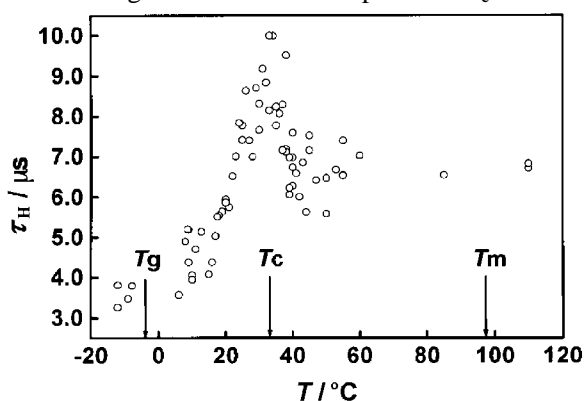


Fig. 5 The relaxation time τ_H of the thermal relaxational mode as a function of temperature

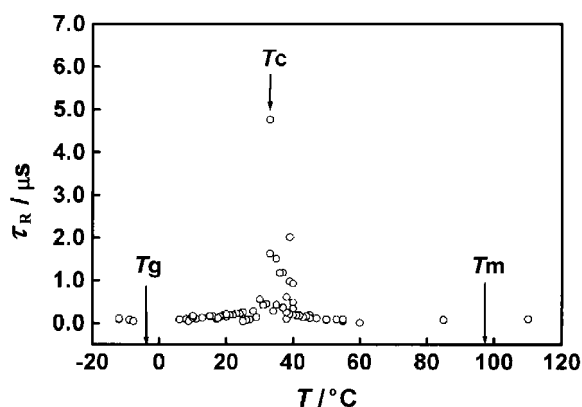


Fig. 6 The relaxation time τ_R of the newly discovered mode as a function of temperature

dependence of τ_R is very different from that of the relaxation time τ_α of the α relaxation studied by dielectric measurement; τ_α diverges at T_g [3]. This means that the newly discovered mode can not be assigned to the α relaxation. Though we have not had an appropriate explanation for the physical origin of the newly discovered mode, the mode must have an important information on the dynamics of the ergodic to non-ergodic transition.

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