The anhydrous solid trehalose: Low-temperature EPR study of glassy and boson peak modes

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ABSTRACT

Electron spin–lattice relaxation times (T_1) were measured by X-band electron paramagnetic resonance (EPR) spectroscopy in irradiated trehalose glass (TR-G) and trehalose-β crystalline state (TR-C) from 5 to 290 K. Throughout the whole temperature interval studied, a consistently shorter T_1 was observed in TR-G than TR-C while the largest difference was detected below ca. 80 K. Here, the theoretical analysis within the soft potential model pointed to the two mechanisms responsible for a more efficient energy exchange between the spin system and the lattice in TR-G: the thermally activated dynamics of glassy modes and the Raman process with boson peak (BP) modes. In this context, the glassy polymorph of anhydrous trehalose corroborates the idea that the boson peak, being a universal property of amorphous/disordered solids, can be studied by EPR even at X-band frequencies. It is further suggested that the mechanisms, involving glassy/soft/BP modes, which provide additional channel for the electron spin coupling with the lattice in glassy as compared to the crystalline state, could be proposed as a universal phenomenon aiming to explain the electron spin relaxation in disordered matrices at temperatures above a few Kelvin in general.

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1. Introduction

Trehalose, a glass-forming disaccharide found in nature (Fig. 1), exhibits the unusual bioprotective properties like anhydrobiosis or cryoprotection [1]. These phenomena, still not completely understood, are often investigated relative to the structural and dynamical properties of trehalose in various solid-state realizations [2–4]. In addition, it has been proposed that trehalose can serve as a model for the hydrogen-bond network described by the axiomatic theory of ideally glassy network [3]. Unlike low temperature crystalline structure, well described by Debye theory [5], the existence of low-frequency modes discovered in glassy state is considered as an unsolved problem of condensed matter physics [6,7]. In this context, the search for the experimental evidence and understanding of the so-called boson peak (BP) excitations, an enhancement of low frequency states relative to an elastic continuum Debye vibrational density of states, has challenged contemporary experimental techniques and theoretical approaches [8–10]. It is assumed that, being a universal property of glasses, the understanding of BP phenomenon can additionally contribute to the clarification of peculiarities of the glass transition itself [11].

This study has been motivated by the fact that trehalose exhibits the highest glass transition temperature, $T_g \approx 403$ K, and the best-developed boson peak of saccharides. Therefore, it allows the investigation of molecular dynamics in the solid state within the large temperature interval. In addition, trehalose is interesting in the context of low-temperature anomalies of glasses related to the impact of hydrogen-bonded network. In this respect the essential advantage of using trehalose as a model system is in the possibility to perform measurements in crystalline and glassy state of the very same molecular compound, an issue not often encountered in the literature [9,12,13].

The application of conventional X-band (≈ 10 GHz) electron paramagnetic resonance (EPR) spectroscopy in the study of BP phenomenon has presented very few results [12,14,15] due to the fact that the probing frequency only partly overlaps the BP frequency range. Nevertheless, as we have shown previously, the analysis of the coupling of the electron spin with the excitations of the lattice can provide a signature of the BP involvement [16]. In this respect the measurement of the effective electron spin–lattice relaxation time (T_1^*) at the local paramagnetic probe level can be considered as being analogous to the specific heat evaluated from calorimetric data [17]. Since the BP effects have been carefully studied by the later technique [18], here we have chosen to focus on T_1^* measurements. In this type of the experiment one addresses the energy exchange between the spin system and the lattice, which is affected by excess in the vibrational density of states in glassy versus crystalline material. It should be mentioned that an alternative approach is focused on the analysis of electron spin–spin relaxation time in glassy solids [19] corroborating
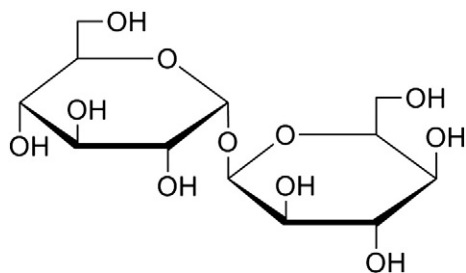

Fig. 1. Chemical structure of trehalose.

the finding of a transition to the new type of dynamics below 20 K [20].

Here we present the comparative study of dynamical properties of trehalose glass (TR-G) and anhydrous polycrystalline trehalose-β state (TR-C) using pulsed X-band electron paramagnetic resonance (EPR) spectroscopy. Due to the fact that trehalose is diamagnetic, the radiation-induced paramagnetic centers [21] are used to study the coupling of the electron spin with the lattice as a function of the frozen-in disorder [12]. T_1^* is presented in the large temperature interval, from 0.012 T_g to 0.73 T_g, indicating more efficient energy exchange between the spin system and the lattice for the paramagnetic defects embedded in the glassy than trehalose-β crystalline state. The experimental evidence is provided showing that the largest difference between the former and the latter state of the host matrix is observed below ca. 80 K. The theoretical analysis of the experimental data is derived within the soft potential model (SPM) [22,23] and the importance of disorder modes in explaining low-temperature properties of glassy state discussed. In this temperature range, which corresponds to the energy region from 2 to 5 meV, boson peak is often detected in Raman and neutron scattering spectra of amorphous solids [2,24]. In this context we relate here a presented experimental data to the BP excitations affected by trehalose hydrogen-bond network properties.

2. Material and methods

α,α-Trehalose (99%) was obtained as trehalose dihydrate (TR-D) from Sigma-Aldrich and used as received. The anhydrous β-crystalline form (TR-C) was prepared by keeping TR-D in an open flask under vacuum (500 mbar) and 403 K for 4 h as described [25]. No difference with respect to the commercially available anhydrous β-crystalline polymorph from Acros Organics was detected. The glassy state of trehalose (TR-G) was prepared by fast quenching of the TR-C melt (488 K) to the room temperature.

Differential scanning calorimetry (DSC) was used in order to verify the crystalline and glassy state of the samples. Calorimetric measurements were carried out using Mettler Toledo 822e differential scanning calorimeter, equipped with Apollo 100 liquid nitrogen cooling system. DSC experiments were conducted on trehalose samples weighting between 5 and 15 mg, placed in aluminum DSC pans and sealed with a pierced lid. All DSC thermograms were obtained at a scan rate of 20 K min^{-1}. During the measurements the calorimeter was flushed with nitrogen gas at a 25 ml/min.

The irradiation treatments of trehalose samples were carried out at room temperature using γ-ray irradiation from ^{60}Co as the radiation source. Irradiation dose of 10 kGy was applied at a dose rate of 3.2 Gy/s, which falls in the suitable EPR response in terms of signal intensity [26]. Subsequently, the samples were annealed at 313 K for three days to secure the stability of paramagentic signal for longer time period [21], loaded into quartz EPR sample tubes (i.d. 3 mm) and sealed under argon.

EPR experiments were performed using Bruker E-580 Fourier transform continuous wave (FT/CW) X-band spectrometer equipped with an Oxford Instruments temperature unit ($\pm$0.1 K). Spin–lattice relaxation times were determined by inversion recovery using an

echo detection sequence with the pulse separation time of 200 ns and π pulse duration of 48 ns. As shown and discussed previously [27], the effective electron spin–lattice relaxation time (T_1^*) was deduced from a biexponential fit of the magnetization recovery curves wherein only the longer component was considered an approximation T_1.

3. Results

In our previous work we have shown that glassy or disorder modes can be detected using EPR spectroscopy since they can affect an energy exchange between the electron spin and the lattice [23]. When present, they can modulate the spin–lattice relaxation of paramagnetic center incorporated in diamagnetic amorphous material in terms of thermally activated relaxation of double-well systems and phonon-induced relaxation of boson-peak/quasi-harmonic local modes. Here we proceed with the analysis considering different paramagnetic centers and take the advantage of high T_g of trehalose to study properties of glassy versus crystalline state within the much broader temperature interval than before [12].

Two trehalose samples exhibiting different degrees of molecular disorder, TR-C and TR-G, were checked by DSC in order to verify the assumed physical state. Thermograms were compared with respect to the physical transformation of trehalose dihydrate upon heating (Fig. 2).

The first thermal event observed while heating trehalose dihydrate from 300 K appears in the DSC curve as an endothermic peak at about 373 K. It can be assigned to the water loss from TR-D [25,28]. Subsequently, a broad endothermic peak follows in the temperature range from ca. 383–413 K attributed to the melting of crystals formed during an intermediate crystallization [28]. The anhydrous β-crystalline trehalose, formed after dehydration as a highest temperature stable polymorph, melts above 450 K as indicated by endothermic peak centered at ca. 488 K. Therefore, TR-C is verified by the thermogram consisting only of this later peak (Fig. 2b) whereas thermogram displaying flat baseline except for the temperature interval around 390 K (Fig. 2c) is typical for TR-G [28,29].

The analysis of radiation-induced paramagnetic centers in solid trehalose both with respect to the underlying molecular reactions and identification of free radical species is still in progress [30]. Due to the complex radiation chemistry various EPR techniques supported by theoretical calculations were attempted and provided data for trehalose dihydrate single crystals, TR-D [31,32]. Here we focus on anhydrous trehalose and present the electron spin echo amplitude during a magnetic field sweep through the EPR spectrum of irradiated TR-G and TR-C (Fig. 3).

Experimental data shown in Fig. 3 indicate participation of at least several radical species, which to the best of author's knowledge, have not been assigned so far for anhydrous trehalose. In order to compare electron–spin lattice relaxation time measurements, T_1^* was detected close to the central field position. Here, larger difference between the electron spin–lattice relaxation data of anhydrous polymorphs of trehalose was detected as compared to the low/high field parts of the spectra pointing to the radicals more intensively coupled with the host matrix [33]. Based on the irradiated TR-D studies [30] some type of carbon centered radical could be assumed. The measurements of T_1^* in TR-C and TR-G were performed in the temperature interval from 5 to 295 K (Fig. 4).

It can clearly be seen from Fig. 4 that throughout the whole temperature interval studied, the electron spin–lattice relaxation rate measured in trehalose glass is larger than in crystalline state i.e. the energy exchange between the electron spin system and the lattice is more efficient in the former than in the latter state of the host matrix. Difference in T_1^* increases upon cooling down both solid trehalose samples and reaches ca. factor of 2 at the lowest temperatures studied.