# Comparative dielectric studies on two hydrogen-bonded and van der Waals liquids

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Broadband dielectric measurements were performed in a wide range of temperatures on glucose, maltose, and their acetyl derivatives. We have indicated that molecular dynamics above and below the glass transition temperature differ considerably for the hydrogen-bonded and van der Waals systems. We have shown that structural relaxation dispersions of D-glucose and maltose are broader than those obtained for peracetyl carbohydrates. Moreover, glass transition temperatures of the former systems are much higher than for the latter ones. In the glassy state of both glucose and its acetyl derivatives only one well-separated secondary relaxation process was identified. In the case of maltose and peracetyl maltose a completely different situation was observed. In the former carbohydrate two secondary modes were detected, whereas in the latter one only a faster relaxation process was visible in the glassy state. This finding is discussed in greater detail on the basis of density functional theory calculations.

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## I. INTRODUCTION

Hydrogen bonds (HBs) are one of the most common interactions occurring in polar and natural systems. HB can be found in proteins, carbohydrates, and water as well as in other chemicals and is responsible for the correct functioning of all living organisms. Hydrogen bonds also play a very important role in stabilizing the native structure of proteins during freeze drying [1–4]. It was shown that the application of highly hydrogen-bonding saccharides, such as sucrose or trehalose prevents the aggregation and inactivation of proteins. It has been proven that the formation of the HB between a given protein and disaccharide prevents the occurrence of such unwanted processes. Hydrogen bonds may also have a great impact on the kinetics and mechanism of some chemical reactions which can be triggered by the proton transfer [5–7]. A good example of such a reaction is tautomerism, which is observed in many substances including saccharides and drugs [8–13].

The average energy that has to be applied to break one $O^{-}H$ hydrogen bond is equal to 19 kJ/mol [14]. It does not seem like much, but on the other hand, HBs have a great impact on the basic physicochemical properties of crystals, liquids, and glasses. The best illustration of this is the water molecule. Many of the essential and unique properties of water are strongly connected to hydrogen bonds.

HBs also determine the dynamics of molecules in the liquid and glassy states. This effect has been widely investigated by NMR, mechanical, or dielectric measurements. In many cases the presence of hydrogen bonds can be revealed by standard measurements. It is noteworthy that in monohydroxyalcohols an additional Debye relaxation, slower than the structural process, can be found in the loss spectra [15–19]. Current interpretation of the molecular origin of this process is still a subject of heated discussion. Some authors claim that it originates from the clusterlike structures while others associate it with the Maxwell Wagner Sillars relaxation [18]. On the other hand, Feldman *et al*. assigned the Debye-type relaxation to the formation of linear chains via hydrogen bonds [20]. In spite of the fact that no consensus has been reached as yet, it is generally accepted that hydrogen bonds are responsible for the slow exponential relaxation process. Hence, one can conclude that Debye relaxation reflects the dynamics of the HB. Consequently, it can be used to probe their dynamics. This finding is of great importance since it gives a new possibility of direct testing of the effect of pressure on the dynamics of the hydrogen bonds. In this context it is worth mentioning that the first such studies showed that the amplitude of the Debye process decreases with increasing pressure. That was interpreted as being caused by the change in the population of hydrogen bonds [19,21].

Moreover it should be added that a slow mode of an almost exponential response function can also be found in the real part of complex permittivity of six carbon monosaccharides. On the basis of the comparison between IR and dielectric data it was concluded that this process is also connected with the hydrogen bonds [22,23].

A significant difference in molecular dynamics between hydrogen-bonded and typical van der Waals liquids is clearly visible in high pressure measurements. It is well known that the structural relaxation process in the former systems, unlike the latter ones, exhibits a weak sensitivity to pressure. Consequently, the $dT_g/dp$ coefficient has a small value within the range of 30–90 K/GPa [24]. For comparison, $dT_g/dp$ is higher than 150 K/GPa for typical van der Waals liquids. Another characteristic feature of the H-bonded systems is the breaking of the time-temperature-pressure superpositioning rule (TTP). On the basis of many studied cases it has been ascertained that TTP works well in almost all nonassociating liquids [25]. On the other hand, this rule does not apply in the case of a liquid-forming network [25]. The explanation of this finding seems to be simple. Various temperature and pressure conditions must surely affect the population of hydrogen bonds. Thus, the structural processes having the same $\tau_\alpha$, measured at different thermodynamical conditions, have to differ in the distribution of their relaxation times.

In this paper we present the dielectric studies of four carbohydrates, namely, glucose, peracetyl glucose, maltose, and peracetyl maltose. The former and the latter systems have the same architectonic backbone. However, they differ in the molecular interactions occurring between the molecules. In D-glucose and maltose, hydrogen bonds determine the molecular dynamics, whereas in the acetyl derivatives, mainly van der Waals interactions occur. We have shown that hydrogen bonds have a great impact on the dynamical properties of the liquid and glassy states of both the D-glucose and maltose. We have demonstrated that basic parameters describing the dynamics of the structural relaxation process differ significantly, depending on the sample. We have also observed that the elimination of the hydrogen bonds influences the flexibility of the carbohydrate molecule. On the basis of our dielectric data and DFT calculations we have proved that peracetyl maltose is much more rigid than nonmodified maltose.

## II. EXPERIMENTAL AND COMPUTATIONAL DATA

Anhydrous D-glucose and maltose were supplied by Sigma Aldrich. The purity of the samples was higher than 99%. Peracetyl glucose and peracetyl maltose were synthesized for the purpose of this paper. The purity of these carbohydrates was determined to be greater than 98%. Before measurements each sample was heated up to melting temperature and supercooled rapidly to room temperature. Next, dielectric measurements were performed. Isobaric dielectric measurements at ambient pressure were carried out using a Novo-Control GMBH Alpha dielectric spectrometer ($10^{-2}$–$10^{7}$ Hz). The samples were placed between two stainless steel flat electrodes of the capacitor with a gap of 0.1 mm. The temperature was controlled by the Novo-Control Quattro system with the use of a nitrogen-gas cryostat. Temperature stability of the samples was better than 0.1 K.

Interconversion of acetyl substituent in peracetyl maltose was studied by means of the density functional theory implemented in the ORCA quantum package [26]. The starting structure was obtained by optimizing about 30 random, hand-modeled structures with the AM1 method. The five most energetically stable structures were reoptimized by the B3LYP/6-31G method. A geometry scan was performed for the most stable structure of the chosen five. All geometry optimizations were done on the B3LYP/6-31G level of the theory. In order to check the validity of the transition state, vibration frequencies were calculated numerically. Energy of the stationary states was recalculated on the B3LYP/6-311G(d,p) level of the theory.

## III. DISCUSSION AND RESULTS

### A. Molecular dynamics above the glass transition temperature

Figure 1 presents the dielectric loss spectra measured above the glass transition for glucose, maltose, and their

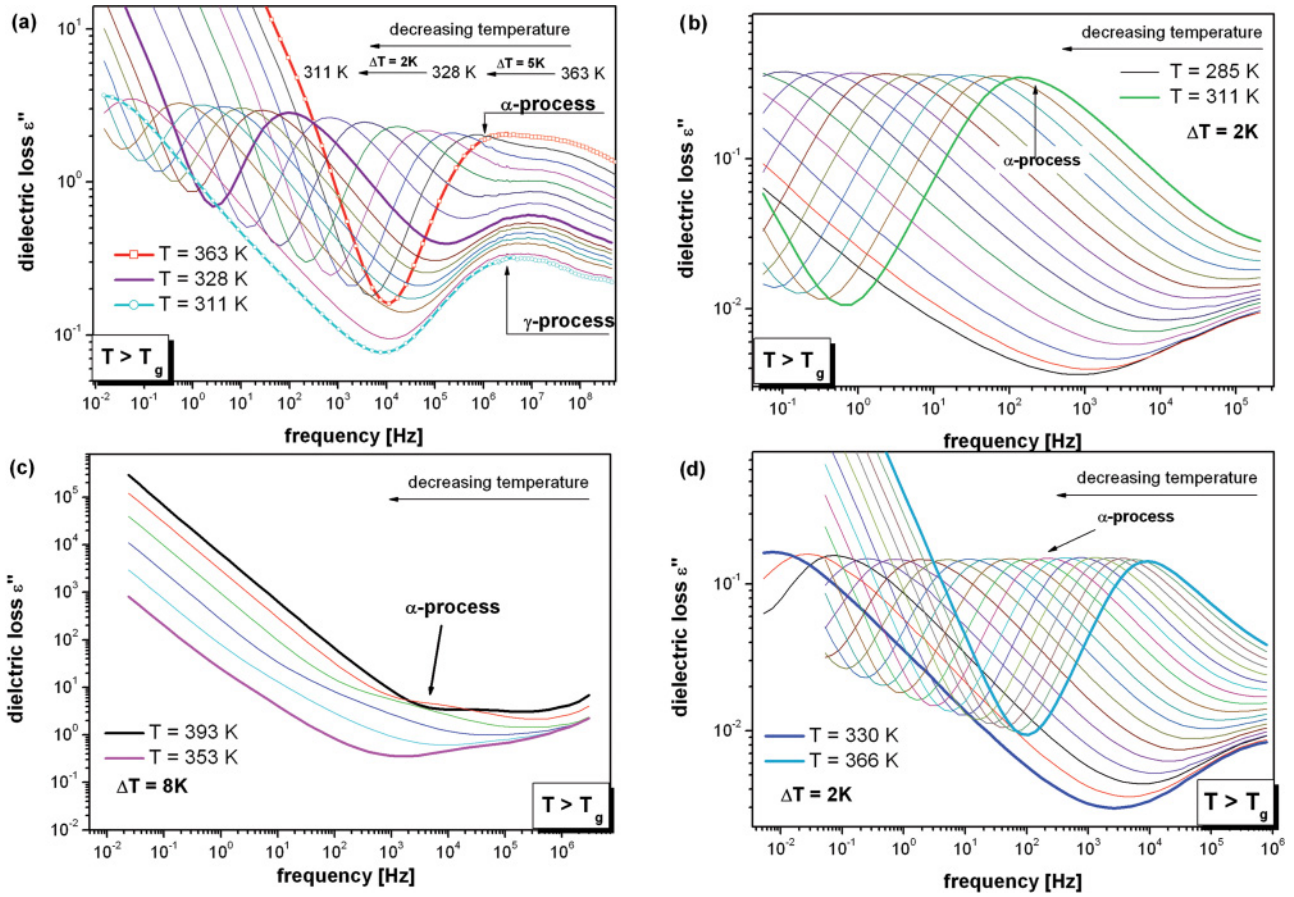



FIG. 1. (Color online) Dielectric loss spectra measured above the glass transition temperature $T_g$ for (a) glucose, (b) pentaacetylglucose, (c) maltose, and (d) octaacetylmaltose.

acetyl derivatives. It is worth mentioning that $T_g$ was defined as the temperature at which the structural relaxation time equaled 100 s. As can be seen, the dc conductivity as well as the structural relaxation process, shifting towards lower frequencies with the decrease of temperature, can be identified for each liquid. It is interesting that in the case of nonmodified (nm) saccharides the contribution of dc conductivity to the loss spectra is significant. Consequently, in the case of maltose the maximum of the $\alpha$ process cannot be observed in the vicinity of $T_g$ in loss spectra. The opposite situation is observed in acetyl derivatives. In these saccharides dc conductivity does not affect the loss spectra to such an extent. Thus, we can see that the substitution of all hydroxyl groups by acetyl units, resulting in the elimination of hydrogen bonds, leads to huge changes in the conductivity of the sample. Furthermore, there is clear evidence that dc conductivity in saccharides originates both from the translational motions of ions, as well as from hopping of the proton in the hydrogen-bonded network as suggested by Crofton and Pethrick [27]. Therefore, we can suppose that the change in dc conductivity is closely related to the destruction of all channels of proton migration in acetyl saccharides.

The other interesting point is the effect of the change in intermolecular interactions on the structural relaxation process in the investigated carbohydrates. To check this we have compared $\alpha$ loss peaks of almost the same $\tau_\alpha$ obtained for glucose, acetyl glucose, and acetyl maltose (see Fig. 2). It can be seen that a scaling plot can be built from spectra measured at completely different temperatures. This means that all samples differ in the glass transition temperature. Additionally, we fitted both structural relaxation peaks to the Kohlrausch-Williams-Watts (KWW) functions

$$\varphi(t) = \exp[-(t/\tau_\alpha)^{1-n}], \tag{1}$$

with the stretching exponent equal to $\beta_{\mathrm{KWW}}\,(1-n) = 0.52$ (glucose), 0.6 (pentaacetylglucose) and 0.55 (octaacetylmaltose), respectively. Hence, it can be seen that the structural relaxation process of glucose is much broader than the one measured for its acetyl derivative. This finding can be explained by referring to the kind of interactions occurring in the examined carbohydrates. It is worth stressing that glucose is a strongly associating liquid and can form networks of different architecture (clusters) which make a sample more heterogeneous. This, in turn, is reflected in a greater distribution of relaxation times of the structural peak for glucose with respect to the one obtained for peracetyl glucose. Unfortunately, we have not been able to compare directly the shapes of the structural relaxation process of maltose and its acetyl counterpart owing to a huge contribution of the dc conductivity to the loss spectra of the former carbohydrate. However, we can use the value of $\beta_{\mathrm{KWW}}$ estimated for trehalose by De Gusseme *et al.* [28]. It is noteworthy that trehalose, similarly to maltose, is a disaccharide consisting of two glucose molecules connected via a different glycosidic linkage. In Ref. [28] authors showed that by using thermally modulated differential scanning calorimetry (TMDSC) it is possible to determine $\beta_{\mathrm{KWW}} = 0.3$ for this disaccharide. Hence, we can be practically certain that the structural relaxation process of nonmodified (nm) maltose is much broader than that measured for the acetyl one.

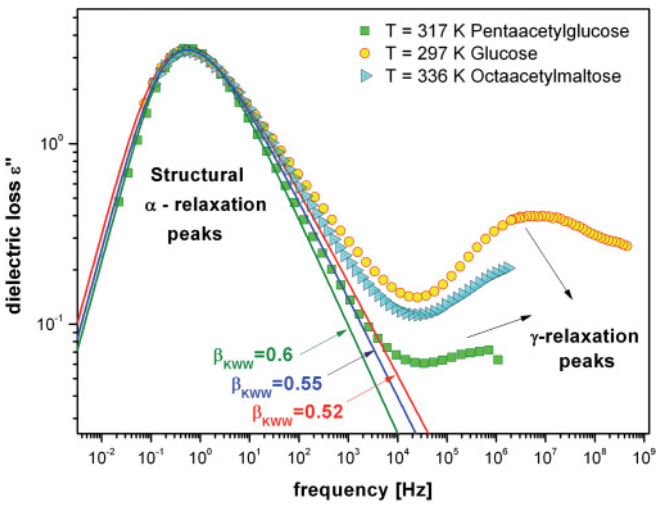



FIG. 2. (Color online) Comparison of the structural relaxation curves obtained at indicated temperatures for D-glucose (○), pentaacetylglucose (■), and octaacetylmaltose (▶). Loss spectra of acetyl glucose and maltose were shifted vertically to superimpose the spectrum measured for D-glucose. Solid lines represent KWW fit with the stretching exponent equal to $\beta_{\mathrm{KWW}} = 0.52$ (glucose), 0.55 (octaacethylmaltose), and 0.6 (pentaacethylglucose).

Moreover, it can also be seen that the structural relaxation process of peracetyl maltose is also broader than that of peracetyl glucose. This experimental fact seems to be consistent with the common rule that the structural relaxation process of compounds belonging to the same family broadens with increasing molecular weight [29–31].

To characterize the molecular dynamics of all investigated carbohydrates dielectric loss spectra presented in Fig. 1 were fitted to the Havriliak-Negami function. It should also be added that in order to extract the structural relaxation times of maltose, the differential form of the Kramers-Kronig (KK) relation was applied.

$$\varepsilon'' \propto -\frac{2}{\pi}\frac{d}{d\ln v}. \tag{2}$$

This approach is very useful in the case of highly conducting samples for which the structural relaxation process is obscured by the dc conductivity. The KK equation links the imaginary and real parts of the complex permittivity and enables a precise estimation of the structural relaxation times. Next, the relaxation map has been constructed (see Fig. 3). Temperature dependences of structural relaxation times were described with the use of the Vogel-Fulcher-Tammann (VFT) equation

$$\tau_\alpha = \tau_0 \exp\left(\frac{D_T T_0}{T - T_0}\right). \tag{3}$$

All fitting parameters are collected in Table I. By using the VFT fits we were able to estimate the glass transition temperatures for glucose, maltose, and their acetyl derivatives. They are equal to $T_g = 307$, 364, 288, and 328 K, respectively. Thus, it can be seen that the glass transition temperature of glucose and maltose is much higher than that of their acetyl counterparts. This finding is consistent with the common rule that highly hydrogen-bonding systems have higher melting, boiling, and glass transition temperatures than the van der Waals liquids.

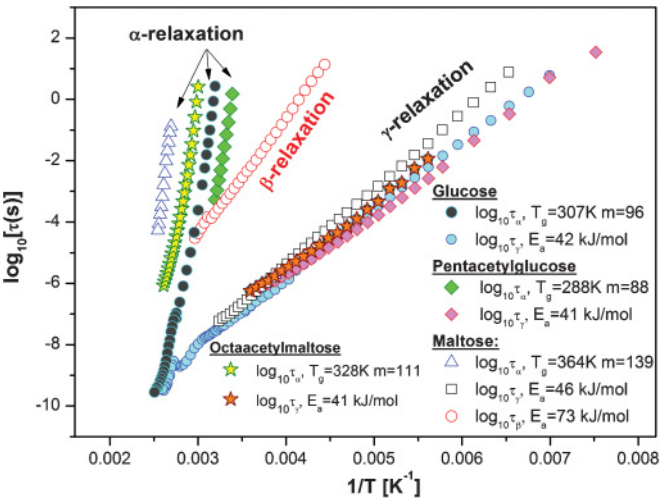



FIG. 3. (Color online) Relaxation map of all investigated carbohydrates.

In the next step the steepness index was calculated from the following equation:

$$m = d\ \log_{10}\ \tau_\alpha / d(T_g/T)|_{(T_g/T)=1}. \tag{4}$$

This single parameter is often used to describe the dynamics of glass forming systems. It provides information about the deviation of the temperature dependence of the structural relaxation times from the Arrhenius behavior. We obtained the fragility values ($m$) 96 (D-glucose), 88 (peracetyl glucose), 111 (peracetyl maltose), and 139 (maltose), respectively. Hence, one can see that nm saccharides are more fragile than their acetyl counterparts. Moreover, we also found that the fragility of the carbohydrates belonging to a given family increases with molecular weight [31].

To summarize, we can state that the dynamics of the supercooled state of nonmodified saccharides differs significantly from the acetyl ones. Here, we report a change in glass transition temperature, fragility, as well as shape of structural relaxation process in these liquids. In the latter part of this work we will focus on the molecular dynamics observed in the glassy state of all the investigated samples.

### B. Molecular dynamics below the glass transition temperature

In Fig. 4 dielectric loss spectra of glucose, maltose, and their acetyl counterparts measured below $T_g$ are presented. Apart from maltose, only one pronounced and well-separated secondary relaxation process was observed which we labeled the $\gamma$ process. On the basis of literature data one can certify or ascertain that this process appears in the whole family of saccharides. It is observed in mono-, di- and polysaccharides regardless of the architecture or structure of the sugar backbone [32]. The main characteristic features of this process in nonmodified saccharides are: (i) the activation energy within the range of 40–50 kJ/mol, (ii) a rapid decrease of dielectric strength with temperature, and (iii) the asymmetric shape of the response function. Moreover, recent research has shown that the considered mode is insensitive to pressure and its relaxation time is independent of the thermodynamic pathways via which the glassy state is obtained [33]. This experimental finding indicates that this mode is related to the intramolecular motions. Indeed, in Ref. [34] it was shown that the $\gamma$-relaxation in saccharides is closely related to the motions of the exocyclic hydroxymethyl unit. Thus, it is of interest to check if the dynamics of the $\gamma$ process is different in pure and acetyl saccharides. To this aim, the $\gamma$-loss peaks were analyzed with the use of the Havriliak-Negami function. The estimated relaxation times of this mode are collected in Fig. 3. Moreover, using the standard Arrhenius equation

$$\tau_\gamma = \tau_0\ \exp\left(\frac{E_a}{k_B T}\right), \tag{5}$$

activation energies of the considered relaxation processes were calculated. Interestingly, the activation energies of this mode were situated within the range of 41–46 kJ/mol for all the examined samples. Hence, $E_a$ of the $\gamma$ process is almost the same, irrespective of the sample.

Moreover, in Fig. 5 superimposed loss spectra measured deep in the glassy state of D- glucose are compared with those obtained for acetyl glucose (upper panel) together with those for nonmodified and acetyl maltose (lower panel). It can be seen that neither the relaxation time nor the shape of this mode change in monosaccharides. Slight changes are observed in the case of disaccharides where the relaxation time of the $\gamma$ process is still the same, whereas the distribution of the relaxation times differs significantly. One can see that the considered relaxation process in peracetyl maltose is much broader than the one in nonmodified disaccharide. It should also be stressed that a considerable difference in amplitude of the $\gamma$- loss peaks in nm and acetyl saccharides is noted. We have also observed that the dielectric strength of this mode is always greater in nm carbohydrates.

At first sight this result might seem to be confusing, since it has been shown that the $\gamma$- relaxation process which

TABLE I. Fitting parameters.

| | | Glucose | Peracetyl glucose | Maltose | Peracetyl maltose |
|---|---|---|---|---|---|
| Structural | log $\tau_\infty$ [s] | −19,15 | −16,46 | −12,85 | −12,16 |
| relaxation | $D_T$ (K) | 15,7 | 5.07 | 4 | 2,07 |
| | $T_v$ (K) | 232 | 226 | 325 | 286 |
| $\gamma$ | log $\tau_0$ [s] | −14,62 | −14.11 | −15.32 | −14 |
| relaxation | $E_a$ (kJ/mol) | 42 | 41 | 46 | 41 |
| Glass transition temperature (K) | | 307 | 288 | 364 | 328 |
| Fragility $m$ | | 96 | 88 | 139 | 111 |

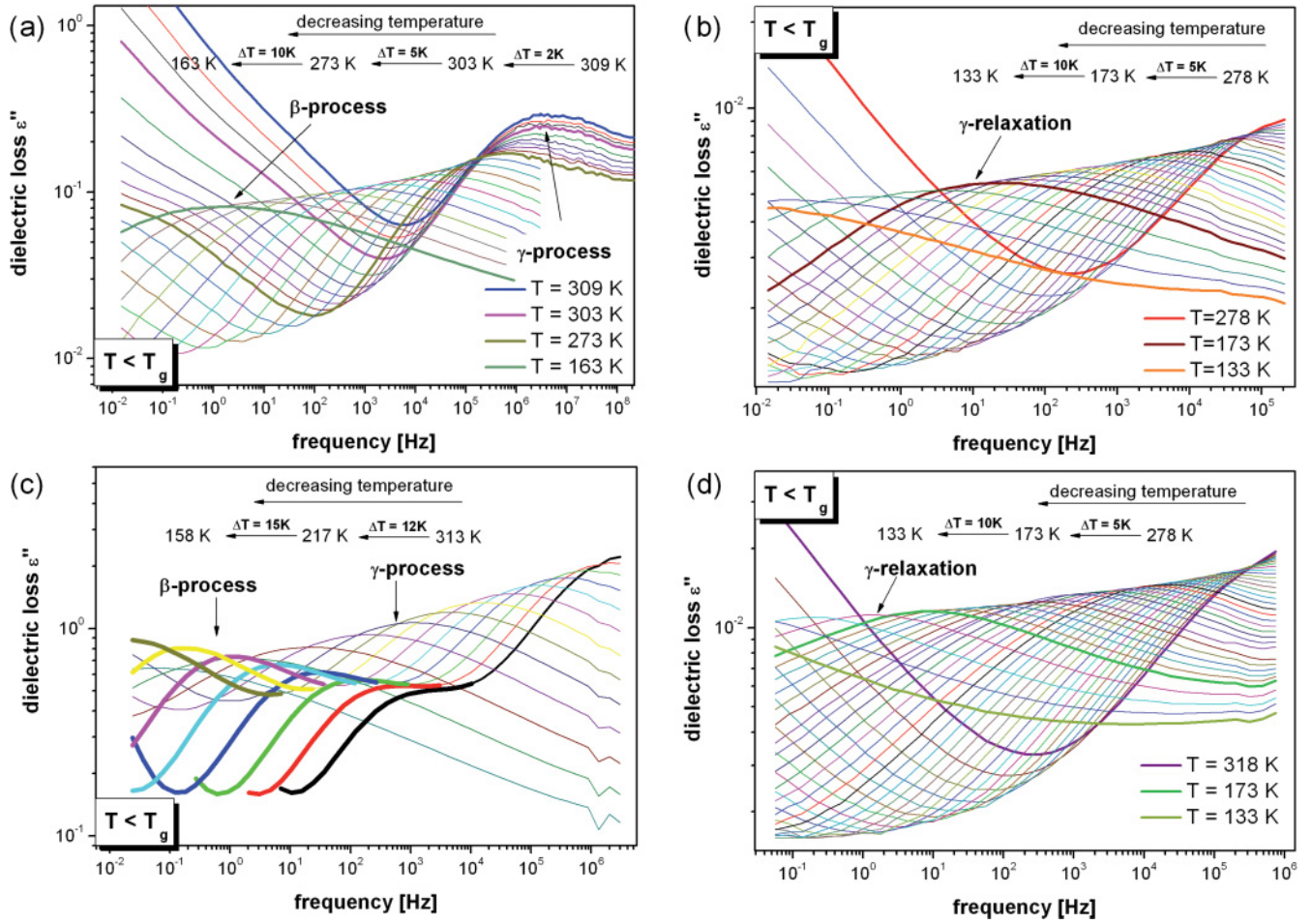



FIG. 4. (Color online) Dielectric loss spectra measured below the glass transition temperature $T_g$ for (a) glucose, (b) pentaacetylglucose, (c) maltose, and (d) octaacetylmaltose.

originates from the motion of the exocyclic hydroxymethyl unit is independent of the character of the sample. On the other hand, it can be expected that the activation energy of this process should change since as it has been proven that the hydrogen bonds have a great impact on the activation energy of this process (see the calculation section in Ref. [34]). However, one can attempt to explain the observed tendencies. As can be seen in acetyl carbohydrate the small hydrogen atom was replaced by a much greater acetyl unit. Hence, one can suppose that the activation barrier which has to be overcome during the motion of the acetyl moiety should be much greater than in the case of $CH_2OH$ group. Therefore, this might be a possible explanation of our finding. To confirm our supposition, further theoretical calculations considering the rotation of the acetyl moiety in peracetyl maltose were carried out.

Every acetyl group is as complex as the hydroxymethyl unit in nonmodified saccharides. In peracetyl maltose there are eight acetyl units, which can rotate independently (see the scheme of the peracetyl maltose structure in Fig. 6). Moreover, rotation of every group is related to the transition between the different energetic minima. In our calculations we have demonstrated the interconversion of one randomly selected acetyl unit with the use of the density functional theory (DFT). In Fig. 6 one can see the diagram which represents the relative change of energy as well as the change of magnitude of the dipole moment during the partial rotation of a selected acetyl group. The geometry scan was calculated on the B3LYP/6-31G level of the theory. The energy of activation calculated with the use of the mentioned method equaled 42 kJ/mol. The activation energy was further recalculated in the higher basis set [6-311G(d,p)]. Its value obtained by the application of a more sophisticated model equaled 40.9 kJ/mol. The received result satisfactorily matches the experimental value of the activation energy. In the diagram in Fig. 6 the change of dipole moment magnitude during the interconversion is also presented. The dipole moment of the acetyl maltose molecule changes significantly during the entire conversion, by more than 2 D. This means that such activity of a molecule should be easily observed by the dielectric spectroscopy method, which is susceptible to dipole moment changes. The pattern of the studied movement is shown in Fig. 6.

It is much more difficult to explain the shape of the $\gamma$-relaxation process which is invariant in monosaccharides, but varies in disaccharides. However, at present we cannot provide a satisfactory explanation for this experimental observation. One can only speculate that rotations of the acetyl moieties attached in different positions to the sugar ring may have

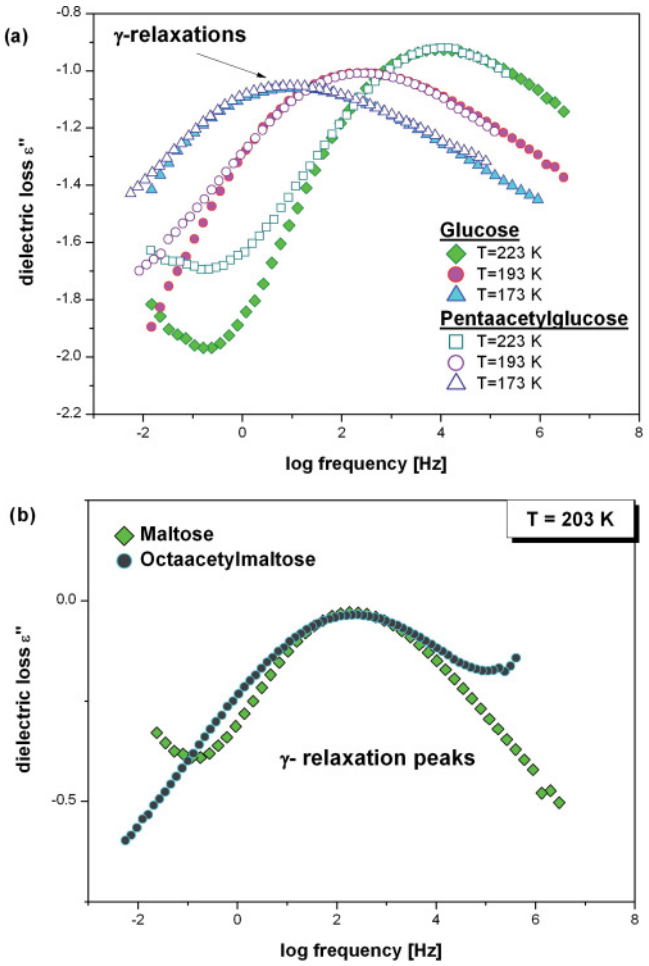



FIG. 5. (Color online) Panel (a): dielectric loss curves measured for D-glucose and pentaacetyl glucose at indicated temperatures. Loss spectra of the acetyl glucose were shifted vertically to superimpose the data measured for D-glucose. Panel (b): superimposed dielectric loss spectra obtained for maltose and octaacetylmaltose at $T = 203$ K. Loss spectra of the octaacetylmaltose were shifted vertically to superimpose the data measured for maltose.

different rates and hence this may have a direct influence on the distribution of the relaxation times of the $\gamma$ peak.

In the final part of this paper we will focus on the dynamics of the $\beta$ relaxation in nm and acetyl saccharides. First of all, it is worth stressing that the slow secondary relaxation process of the Johari-Goldstein (JG) nature can only be seen as an excess wing below the glass transition temperature in D-glucose. Since the structural relaxation process in modified monosaccharides is described by the KWW function with the lower value of $n$ (see Fig. 2) we can expect that the JG process in this carbohydrate will be even less visible in the loss spectra than in D-glucose. This supposition is a direct implication of the coupling model (CM) predictions indicating that separation between structural and JG relaxation processes increases with increasing $n$. One can add that this rule was verified experimentally for different systems [29,35,36].

At this point one can add that CM is a theoretical tool which enables us to estimate the relaxation time of the JG relaxation process. The primitive relaxation time $\tau_0$ of the CM is a good estimate of $\tau_{JG}$. This together with the relation linking $\tau_\alpha$ and $\tau_0$ given by the CM leads to the following equation [37,38]:

$$\tau_{JG} \approx \tau_0 = (t_c)^n (\tau_\alpha)^{1-n}. \quad (6)$$

Here $t_c = 2$ ps for small molecular glass formers and $\tau_\alpha$ and $(1-n)$ are the parameters of the KWW function, based on the stretching exponent derived from the fitting structural dispersion to the KWW function and the structural relaxation time.

In fact, as can be seen in Fig. 4, the excess wing in acetyl glucose is much less pronounced than in the case of D-glucose. This observation confirms the predictions of the CM.

A slightly different scenario was observed in the case of modified and nonmodified disaccharides. Loss spectra presented in Fig. 4 revealed that there are two secondary relaxation processes in the glassy state of maltose, whereas in its acetyl counterpart only one can be seen.

It should be added that a similar observation was made by Sousa *et al.* in the case of polysaccharides cellulose and cellulose acetate. They showed that in the latter system only one secondary relaxation process can be observed while in the former, two can be identified in the loss spectra [39]. At this point we should resort to the molecular origin of this process. Recent pressure measurements have showed that this process is sensitive to pressure; the activation volume of this mode changes from 15 [40] up to 21 $cm^3$/mol [33], depending on the sample. Moreover, it was shown that the $\beta$ process feels the structure of the glass. One can also add that the considered mode moves toward lower frequencies with the addition of water [41]. Hence, based on these simple experimental findings one may have the impression that the $\beta$ process in disaccharides exhibits properties which are characteristic for the structural relaxation process. However, further dielectric investigations supported by computations concerning the activation energy as well as the activation volume showed that this mode originates from the twisting motions of the monosaccharide units around the glycosidic linkage [40]. Summarizing, one can state that the $\beta$-relaxation process in disaccharides is related to the JG relaxation process coupled with the rotation of the monosaccharide units around the glycosidic linkage. Based on the above, one may wonder why there is no signature of the $\beta$-relaxation process in acetyl di- and polysaccharides, To clarify this, one can take into account the coupling model predictions. As was discussed earlier, separation between JG and structural relaxation processes becomes smaller with the lowering of the value of the stretching exponent of the KWW function. Unfortunately we are not able to extract the correct value of $n$ for maltose. On the other hand, we can be sure that the stretching exponent estimated for maltose should be much greater than the one determined for its acetyl derivative ($n =$ 0,45). Hence it can be concluded that the JG process is too close to the structural relaxation to be observed in the loss spectra as a separated peak in the modified disaccharide. The other reason which may explain the lack of the $\beta$ process in the loss spectra measured much below the glass transition temperature for acetyl maltose is the increase of rigidity of the glycosidic linkage. To address this issue, details of the electronic structure

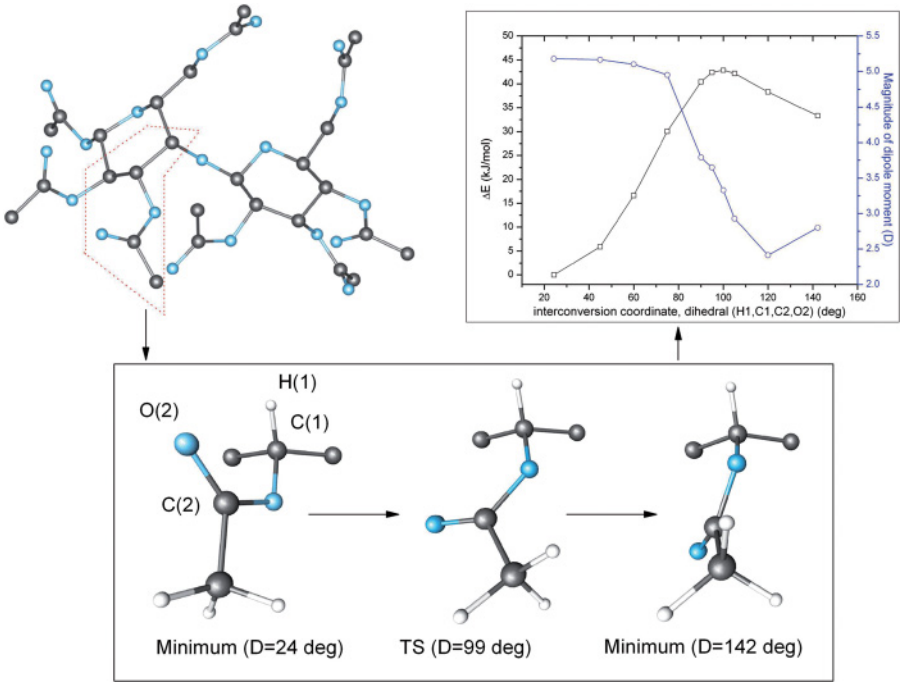
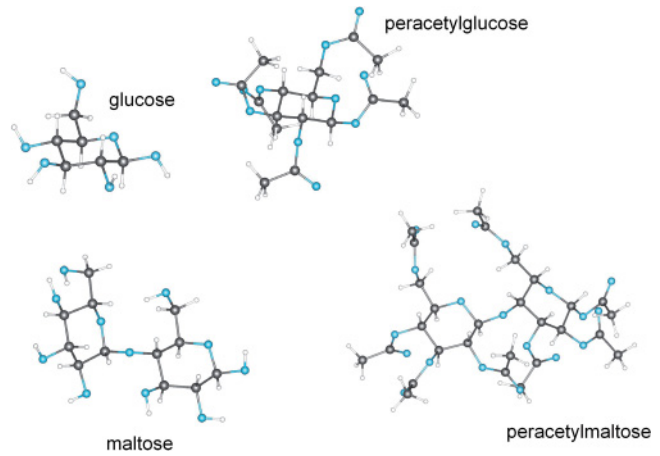



FIG. 6. (Color online) Visual representation of the conformational interconversion related to the rotation of the acetyl unit in peracetyl maltose. Structure of peracetyl maltose was drawn without hydrogens in order to present the image more clearly. All oxygens are colored with light blue and carbons with dark gray. Changes of dihedral angle $D$ (H1,C1,C2,O2) as a function of relative energy are presented in the diagram inset. Transition state has a dihedral angle $D$ equal to 99°.

of nonmodified saccharides and their acetyl counterparts need to be compared. In Ref. [40] rotation of two rings via the glycosidic linkage in maltose was studied by means of DFT calculations. This rotation should be seen as a change of conformation, formed by a jump from one local energy minimum to another. This is possible since nm disaccharides have few stable minima due to two dihedral angles which describe the mutual position of the rings. Moreover, these structures at their minima are stabilized by different patterns of internal hydrogen bonds. The structure of peracetyl maltose differs from the other liquids. In Fig. 6 one can see the structure of peracetyl maltose without hydrogens (hydrogens were not drawn in order to provide a clearer image). Acetyl substituents constitute a great steric hindrance. Moreover, they are not able to form hydrogen bonds which could stabilize certain structures. From this point of view, the allowed area in the peracetyl maltose energy space due to the same dihedral angles as in maltose is much more restricted. In other words, there is only one preferred mutual position of peracetyl maltose rings or there is more than one preferred minimum due to the mutual situation of rings. Moreover, the energy barrier is so extremely high that rotation of monosaccharide units around the glycosidic linkage is practically blocked. Thus, one can suppose that the activation energy of the $\beta$-relaxation process in acetyl maltose is much higher than that calculated for the nonmodified maltose. Consequently, it seems reasonable to expect that the $\beta$-relaxation process is shifted toward lower frequencies and hence is hidden under the high frequency tail of the structural relaxation process in modified maltose.




Scheme 1. (Color online) Structures of the investigated saccharides. Gray symbols, carbon atoms; blue, oxygen atoms; and white, hydrogen atoms.

On the basis of the above, one can certify that due to the restrictions in the rotation of rings via glycosidic linkage, acetyl disaccharides are much more rigid than nm saccharides. On the other hand, the local dynamics in peracetyl maltose seems to be more complicated with respect to the nonmodified saccharides. It is worth recalling here that internal mobility of a single acetyl unit is comparable to the mobility of one exocyclic hydroxymethyl group which is present in nm saccharides. Moreover, we need to bear in mind that there are eight such acetyl groups in peracetyl maltose, whereas in nm disaccharides there are only two hydroxymethyl groups. Therefore, the flexibility of terminal units is greater in acetyl saccharides. However, as it has been pointed out above, mobility of terminal groups is strictly local. Thus, it seems that acetyl di- and polysaccharides are much more rigid than nonmodified saccharides. This finding may open new prospects for these carbohydrates. For instance, acetyl saccharides may be used as a new kind of matrix stabilizing labile amorphous drug or other agents.

## IV. CONCLUSIONS

In this paper four different carbohydrates were investigated. Glucose and maltose are H-bonded liquids, whereas in acetyl

carbohydrates the van der Waals interaction dominates. We have found that dynamics of glucose and maltose differ significantly from that reported for peracetyl glucose and maltose. We have demonstrated that distribution of the structural relaxation times, the glass transition temperature, as well as fragility differ markedly and depend on the character of the examined sample. Surprisingly, the change of the character of intermolecular interactions does not affect the dynamics of the $\gamma$-relaxation mode. Moreover, it has become apparent that this mode has the same activation energy, relaxation time, and shape in glucose and its acetyl derivative, whereas in maltose and peracetyl maltose only the distribution of the relaxation time of the $\gamma$-loss peak changes. This finding was discussed in terms of DFT calculations. We have also shown that there is no trace of a slow secondary relaxation process in peracetyl maltose. This experimental fact was interpreted in view of the increasing rigidity of the glycosidic linkage. We have concluded that due to steric hindrance, the motions of the monosaccharide units around the oxygen bridge become highly restricted. This in turn results in the shifting $\beta$-relaxation process under high frequency wing of the structural relaxation process. Thus, this mode cannot be observed in loss spectra as a separate loss peak in the acetyl di- and polysaccharides. This finding is quite important in view of the potential application of such materials in pharmacology or medicine. It is commonly known that saccharides can be used as cryoprotectants, stabilizers of amorphous drugs, or native structures of proteins. Since acetyl saccharides are much more rigid than the nonmodified carbohydrates and, moreover, are biocompatible, they can also be used as a new kind of matrix stabilizing drug, which is poorly water soluble.

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