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# Kosmotrope character of maltose in water mixtures

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**Abstract**

It is well known that water plays a fundamental role for living beings, because the nature of water transformations provides for the ability to preserve biostructures. Solute can be classified as "kosmotropes" or "chaotropes" depending on the interaction strength with water. In the case of solutes destroying the natural hydrogen bonded network of water, called "kosmotropes" or "structure-makers", the denaturation processes can be inhibited.

The aim of this work is to investigate the vibrational behaviour of maltose/$H_2O$ mixtures in order to characterise the changes induced by the sugar on the $H_2O$ hydrogen-bonded network. The obtained findings point out that maltose has a destructuring effect on the water tetrahedral network and emphasise its kosmotrope character.

*Keywords:* Maltose; Water mixtures; Bioprotection; Vibrational modes; Neutron scattering

## 1. Introduction

Neutron scattering has been demonstrated to be a powerful tool for characterizing the structures and dynamics of biological molecules. Vibrational spectroscopy is one of the most widely used methods for obtaining information on materials irrespective of their state, being equally applicable to the study of gases, liquids, crystals, and amorphous solids. Neutron spectroscopy can be used to provide vibrational spectra which are different from their optical counterparts infrared (photon absorption) and Raman (photon scattering) spectroscopies [1–4]. These differences are connected with the nuclear nature of the atomic scattering potential, which, being insensitive to the ever present electrons, makes the optical selection rules irrelevant. Furthermore, being the magnitude of the hydrogen incoherent scattering cross-section greater than the cross-section of the most other atoms, the neutron response from hydrogen completely dominates the spectra [1–3].

It is well known that water plays a key role in living systems thanks to its unique properties. When liquid water is cooled, it contracts until a temperature of approximately 4 °C is reached; after that, it expands slightly until it reaches the freezing point, and then when it freezes it expands by approximately 9%. The physiological damages induced by ice on the living organisms are due to this expanded structural arrangement that destroys cells and tissues. Cyroprotectants are solutes able to reduce the damage caused by both solution injury and intracellular ice injury, decreasing the intracellular water content without dehydrating the cell [5–7]. Cryoprotectant molecules interacting more strongly with water than with themselves have a strong effect on the tetrahedral coordination network of water, i.e. they affect the structural properties of water by imposing a new order. They are therefore defined to have a "kosmotrope" or "structure-maker" character. Maltose, a cryoprotectant disaccharide, is produced in response to desiccation or freezing by a number of species of plants and animals specifically adapted to survive extreme cold or drought. This cryoprotectant is a partial dehydrant that prevents the formation of ice crystal artefact in frozen tissue sections [7].

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From a molecular point of view, many experimental studies [8–12] have been addressed to understand the cryoprotective mechanisms of maltose also in comparison with homologous disaccharides, showing that maltose is able to create a strong interaction with water, as indicated by the high values of the solute–solvent interaction strength and of hydration number [9], destroying the tetrahedral network of water [8] and producing a slowing down of water dynamics [12].

The present paper is focused on the study of the vibrational properties of water mixtures of maltose investigated by inelastic neutron scattering (INS). Measurements have been performed at $T = 27$ K for four concentration values. A detailed comparison between the maltose/$H_2O$ mixtures and ice at the same temperature is shown. In particular, we obtained information about the modifications induced by maltose in the translational, librational, and bending spectral regions of ice.

## 2. Experimental

Maltose (4-*O*-α-D-glucopyranosyl-D-glucose) is constituted by two pyranose rings of glucose in the α configuration, the oxygen bridge linking the two carbon atoms C1 and C4 of the two rings; the α and β structures of the same monosaccharide differ only in the orientation of the OH groups at some carbon atom in the ring itself (mutarotation equilibria). In its crystalline form maltose presents a monohydrate state ($C_{12}H_{22}O_{11}\cdot 1H_2O$). Maltose is a reducing sugar because the anomeric carbons on the right-hand sugar are part of a hemiacetal and exhibits mutarotation [9].

INS measurements have been performed by using the indirect geometry time-of-flight spectrometer TOSCA at the ISIS Pulse Neutron Facility (DRAL, UK) [4]. The energy resolution of TOSCA is $\Delta E/E \approx 1.5$–2% for energy transfers up to several hundred meV. This high resolution coupled with the high intensity of the ISIS source makes TOSCA ideal for studying the dynamics of water and water mixtures below 2000 $cm^{-1}$ (250 meV) [1–4].

Ultra pure powdered maltose and $H_2O$, purchased by Aldrich-Chemie, were used for the experiment. Measurements were performed at a temperature value of 27 K on hydrogenated maltose ($C_{12}H_{22}O_{11}$) in $H_2O$ at different weight fraction values corresponding to 2, 7, 10, and $14H_2O$ molecules for each disaccharide molecule.

The samples, contained in thin walled aluminium cells, were cooled to 27 K by a liquid helium cryostat. For all the investigated hydrogenated samples, the measurement time was 12 h for each run. Fast cooling rate assured to avoid sample crystallisation, as confirmed by IR tests; furthermore ultrasonic [13] and viscosity measurements [14] indicate that maltose in water solution is strongly bonded to more than ~22 water molecules at room temperature and that this hydration number abruptly increases by lowering temperature. Therefore, at the investigated concentration values, no bulk water is present.

For the data treatment the standard GENIE programme has been used [4]. The multiple scattering contribution has been minimised by using a thin sample in order to obtain a scattering transmission from the sample ⩾90%. The multiphonon neutron scattering contribution (MPNS), which can be significant at high temperature and large momentum transfer, has been calculated directly from the measured spectra by using a method of sequential iterations. Since measurements were performed at low temperature, the MPNS contribution is not large at the translational modes region (i.e. at low Q region) [1–3].

## 3. Results and discussion

Previous INS results on maltose and its homologous [11] emphasised the differences among disaccharide vibrational properties starting by a comparison with the ice spectrum obtained at the same temperature value. In order to analyse the modifications induced by maltose on water, we subdivided the ice spectrum, shown in Fig. 1, in different regions [1–3] which will be selectively discussed. Fig. 1 shows also these spectral regions in the 0–1800 $cm^{-1}$ range of maltose/$H_2O$ mixtures for four concentration values.

### 3.1. 0–400 $cm^{-1}$ region

In Fig. 2 two bands in the ice spectrum are first observed: the first one, having a sharp peak at ~56 $cm^{-1}$, is dominant on the second one centred at ~148 $cm^{-1}$. They can be assigned to acoustic modes. It is known, in fact, that in the ice spectrum the peak at ~56 $cm^{-1}$ denotes the first Van Hove singularity in the dynamics of acoustic phonons. The two peaks present at ~224 and at ~304 $cm^{-1}$ with cutoffs on their right-hand sides are due to molecular optical modes [1–3].

It is observed from Fig. 2 that in presence of maltose the sharp peak of the low energy acoustic modes appears significantly lower and broader and shifted at ~68 $cm^{-1}$. The shift at higher energy is indicative of a strong

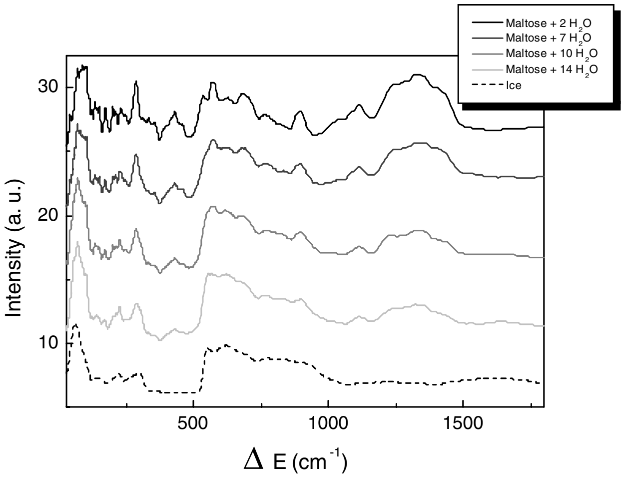

Fig. 1. INS spectra of ice and maltose/$H_2O$ mixtures.