Wetting Effect on Optical Sum Frequency Generation (SFG) Spectra of D-Glucose, D-Fructose, and Sucrose

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Abstract

We report a sum frequency generation (SFG) spectroscopy study of D-glucose, D-fructose and sucrose in the C-H stretching vibration regime. Wetting effect on the SFG spectra was investigated. The SFG spectrum of D-glucose changed from that of α-D-glucose into those of α-D-glucose monohydrate by wetting. The SFG spectra showed evidence of a small change of β-D-fructopyranose into other anomers by wetting. SFG spectra of sucrose did not change by wetting. Assignments of the vibrational peaks in the SFG spectra of the three sugars in the dry and wet states were performed in the C-H stretching vibration region near 3000 cm^{-1}.

Keywords: Optical sum frequency generation (SFG) spectroscopy, glucose, fructose, sucrose, C-H stretching regime

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1. INTRODUCTION

In optical sum-frequency generation (SFG), photons at two different frequencies illuminate the sample and ones at the sum frequency are emitted. It is a second-order nonlinear optical process and occurs in media with structures lacking inversion symmetry at the moleculear level and does not occur in media with inversion symmetry [1]. It is enhanced when one of the incident two frequencies is in the infrared region and is resonant with the vibrational frequency of the molecules. Due to this selectivity for symmetry and molecular vibrations, SFG has been found to be useful to study not only surfaces and interfaces [2-5] but also biomaterials [6]. Biomaterials consist of various kinds of chiral molecules and have structures lacking inversion symmetry at the molecular level. Thus, they can generate SFG light by resonant excitation of the molecular vibration [7]. There are various studies on biomaterials by using SFG spectroscopy and imaging microscopy [6,8,9]. In order to promote the analyses of biomaterials by the SFG techniques, it is necessary to accumulate SFG data of pure saccharides.

As a very first step of such effort, we chose D-glucose, D-fructose and sucrose as the samples in this study. The crystal structures of D-glucose and D-fructose belong to the chiral group of $P2_12_12_1$ and that of sucrose belongs to the chiral group $P2_1$. Chiral molecules do not have inversion symmetry, so SFG signal can be generated from the bulk of these materials. These three sugars are light-weight-molecule saccharides contained in biomaterials as energy storage. They are also important in food and pharmaceutical applications [10,11]. Figure 1 shows the structures of the anomers of D-glucose and D-fructose together with the structure of sucrose.

D-glucose is the most common saccharides and exists abundantly in two forms as α-D-glucopyranose (Fig. 1(a)) and β-D-glucopyranose (Fig. 1(b)). D-fructose occurs widely in nature and is known to be the sweetest of the naturally occurring sugars. In crystalline state, D-fructose exists only in the β-D-fructopyranose form (Fig. 1(d)). Sucrose (Fig. 1(g)) is a disaccharide

consisting of two mono-saccharides, i.e. α-D-glucopyranose and β-D-fructofuranose (Fig. 1(f)), connected by a glycosidic bond [12]. When D-glucose and D-fructose are dissolved in water, the mutarotation takes place. At the equilibrium, D-glucose exists in two forms as 36 % α-D-glucopyranose and 64% β-D-glucopyranose [13], while D-fructose exists in four forms as 60% β-pyranose, 30% α-furanose (Fig. 1(e)), 10% β-furanose and a negligible amount of α-pyranose (Fig. 1(c)) anomers [11].

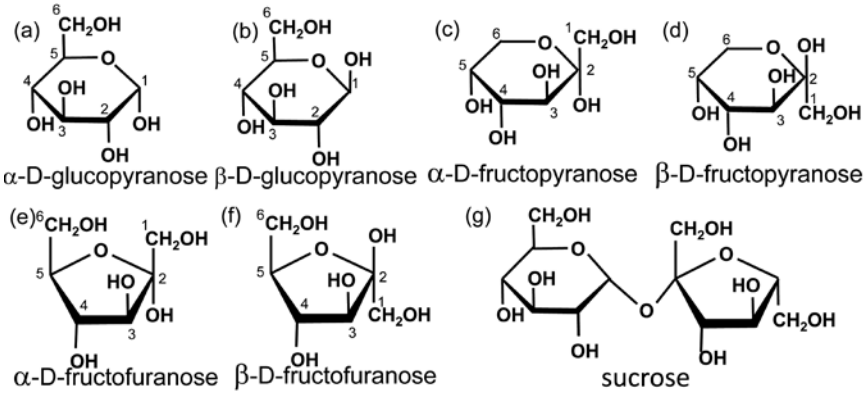

Fig. 1 Molecular structures of the anomers of D-glucose (a,b) and D-fructose (c-f) and the molecular structure of sucrose (g). The numbering of carbon atoms are based on Ref. [10].

There have been various vibrational spectroscopy studies of the three sugars [14-19]. Longhi and coworkers reported IR and Raman spectra of D-glucose and some deuterated derivatives to assign bands in the CH region [18]. Ibrahim et al. performed FTIR absorption measurement and DFT calculation to analyze the structure of glucose and fructose [17]. Wermeir and coworkers reported ATR-FTIR study of sugars containing mainly D-fructose and D-glucose in tomato as an "optical tongue" for classification of main taste components of tomato [19]. On the other hand, using SFG method, there have been studies only of D-glucose among the three sugars. Miyauchi et al. reported SFG spectra of D-glucose with polarization of incident IR and visible beams parallel to each other [6,20]. These SFG measurements of D-glucose did not specify the

anomers of D-glucose and moisture effect on the SFG spectra. There has been no SFG study of fructose and sucrose.

We are motivated to develop the SFG system as a tool for detecting and quantifying sugars contained in fruits and foods [21]. Especially, the fine structures of the C-H vibration peaks around 3000 cm^{-1} are expected to give information on the configuration of CH groups in the saccharides. For that goal, it is necessary to elucidate the characteristic of SFG spectra of D-glucose, D-fructose and sucrose. Because the sugars exist in biomaterials in wet state, the water content is also very crucial. The water content was also found to affect the sweet taste of the sugars [14]. In this study, we report on SFG spectroscopy of the three sugar materials, D-glucose, D-fructose and sucrose in dry and wet states in the C-H stretching regime around 3000 cm^{-1}. By using different polarization combinations, spectra are expected to give more detailed characteristics of the sugars.

The SFG intensity at frequency $\omega_{SFG} = \omega_{vis} + \omega_{IR}$ is given as:

$$I(\omega_{SFG}) \propto \left|\chi_{eff}^{(2)}\right|^2 I(\omega_{vis}) I(\omega_{IR}) \qquad (1)$$

Here $\chi_{eff}^{(2)}$ is the effective second order nonlinear susceptibility, and $I(\omega_{IR})$ and $I(\omega_{Vis})$ are the intensities of the IR and visible fields. The effective susceptibility is proportional to the Raman tensor $M_{\alpha\beta}$ and IR tensor A_γ as the equation below [22]:

$$\chi_{eff}^{(2)} = \frac{N \sum_{\alpha,\beta,\gamma} \left\langle M_{\alpha\beta} A_y \right\rangle}{\varepsilon_0 \left(\omega_{IR} - \omega_q - i\Gamma_q\right)} \qquad (2)$$

Here N is the density of the molecules in unit volume, $\left\langle M_{\alpha\beta} A_y \right\rangle$ is the macroscopic average of the molecular hyper polarizability $\sum_{\alpha,\beta,\gamma} M_{\alpha\beta} A_y$, ε_0 is the vacuum premittivity, ω_q is the molecular vibrational frequency, and Γ_q is the line width of mode q. From Eq. (2), we can say that a medium can generate SFG signal when both IR absorption and Raman scattering are active.

2. EXPERIMENTAL

Commercial D-glucose, D-fructose and sucrose crystalline powders were purchased from Wako pure chemical industries, Ltd. They were kept in rectangular quartz cells of sizes 45x12.5x4.5 mm^3 with two parallel windows transparent from the wavelength 200 nm to 3500 nm. The cells were sealed by plastic tapes. Since the samples are in powder forms, the orientation of their crystal axes is regarded as random.

In order to moisten the sample with water, we used a glass chamber of 12 cm height. The powder sample was put at a position ~10 cm higher than the bottom of the chamber. Pure water of temperature ~ 40°C filled the one-fourth height of the chamber. A cap was put on the mouth of the chamber to keep the vapor in the chamber. The vapor from the 40°C water rose up and moistened the powder. The amount of water absorbed by the powder was a function of the time and was determined by using a scale AUX220 (Shimadzu) with accuracy of 0.1 mg. After measuring the weight of the water content, the samples were kept in quartz cells. In order to dry the sample we used a drying oven DS64 (Yamato Scientific) set at 50°C. The drying time was about 5h.

The SFG spectroscopy system was built as shown in Fig. 2. We used doubled-frequency light pulses at visible wavelength 532 nm with the time width 30 ps and the repetition rate of 10 Hz generated by a mode-locked Nd^{3+}:YAG laser. Tunable infrared light pulses at wavelength of ~ 3 μm was output from an optical parametric generator with an amplifier system pumped by the fundamental and SHG output of the same Nd^{3+}:YAG laser. The pulse energy of the visible light was from 10 μJ to 40 μJ and that of the infrared (IR) was about 150 μJ at the sample. The spectral width of the IR light was 6 cm^{-1}.

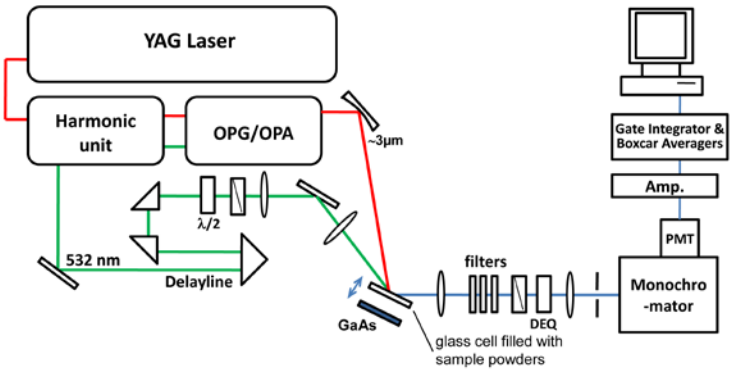

Figure 2: Experimental setup for sum frequency generation spectroscopy

We used a concave mirror two-dimensionally tilted automatically by a computer, in order to adjust the IR light reaching exactly the same position on the sample cell window as the visible pulses. A delay line was used to adjust the temporal overlap of the IR and the visible pulses. The visible and infrared beams reach the sample with incident angles of 75° and 45° with respect to the normal to the cell window plane, respectively. The SFG light was collected at the reflective angle of 70°. Near the entrance slit of the monochromator, band pass filters (Asahi SV0490) was used to damp the excitation visible and infrared light beams. Then a depolarizer plate (Sigmakoki DEQ-1N/180-3500) was put to remove the polarization dependence of the sensitivity of the monochromator. We replaced automatically the main sample with a reference GaAs(001) sample in each measurement. The SFG signal of the reference sample was used to normalize the SFG of the sample. SFG spectra of each sugar were taken from 2800 cm^{-1} to 3050 cm^{-1} with a scanning step of 5 cm^{-1}. The accumulation for each point was done for 200 laser shots. Each measurement was conducted in four polarization combinations as SPP (SFG in s-polarization, visible in p-polarization and IR light in p-polarization with respect to the incident plane), PPP, SSP and PSP.

First the SFG measurement was performed for dry samples of D-glucose, D-fructose and sucrose. Then wet samples were observed. The time for one measurement was from 60 to 90 minutes. All experiments were carried out in air at 21°C.

3.1 D-glucose

Two anomers of D-glucose, namely α-D-glucopyranose and β-D-glucopyranose have the same chemical structure, but differ in the arrangement of bonds around C(1) as shown in Figs. 1(a) and (b). Here C(1) is the part of the aldehyde group H(C=O)- in the open chain form of the D-glucose molecule [10] and the number in the parenthesis is the number of the carbon as shown in Fig. 1. The OH group at the C(1)-OH bond and the – $C(6)H_2OH$ group are on the opposite side of the ring plane for the α-anomer, whereas they are on the same side for the β-anomer [10]. According to Longhi and coworkers, another important difference between α- and β-D-glucopyranoses is that α-anomer has *gt* conformation with O(5)-C(5)-C(6)-O(6) in *gauche* configuration and C(4)-C(5)-C(6)-O(6) in *trans* configuration, while β-anomer has *gg* conformation for the corresponding atoms [18].

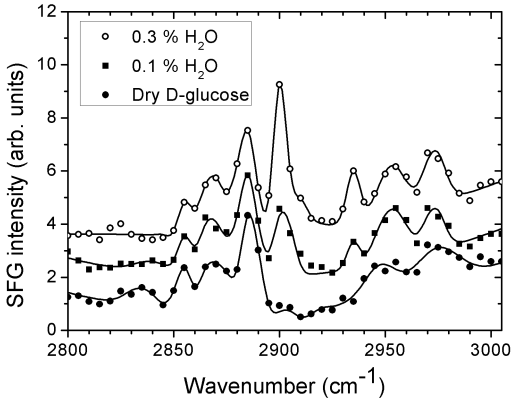

Figure 3: SFG spectra of D-glucose with 0%, 0.1%, 0.3% H_2O for the polarization combination of SPP. Lines are multiple Gaussian functions fitted to the experiment. The zero levels of the spectra are displaced in the vertical direction for convenience to the eyes.

Figure 3 shows the SFG spectra of D-glucose with 0% (line with closed circles), 0.1% (line with closed squares) and 0.3% (line with open circles) water content for the polarization combinations SPP. We performed the experiment in four polarization combinations as PPP, SPP, SSP, and PSP, but the four spectra had the same shapes for each of wet and dry samples. The 0% curve in Fig. 3 shows peaks at 2870 cm^{-1}, 2885 cm^{-1}, 2905 cm^{-1}, and 2955 cm^{-1} roughly consistent with the Raman data by Corbett et al. [15]. Since 96-97% α-anomer is contained in the dry sample, the features of the curve with closed circles is attributed to α-D-glucopyranose. The contribution of small percentage (3-4%) of β-D-glucopyranose in the sample might be negligible in the spectra.

Table 1 lists the assignment of the SFG bands of dry and wet D-glucose. We note that for each vibrational peak all the atoms vibrates more or less generally and the "assignment" indicates the part of the molecule with relatively the largest amplitude of motion. The peak at 2955 cm^{-1}can be assigned to an asymmetric CH_2 stretching modes [15]. The peaks at 2885 cm^{-1}may be assigned to a CH stretching mode [15,18]. Ref. [15] reports that it is an asymmetric CH stretching mode at the C(6)-H-C(5)-H bond.

According to the β-D-glucose data of Corbett et al., the peak at 2900 cm^{-1} in the SFG spectra in Fig. 3 can be assigned to the C(6)-H-C(5)-H symmetric stretching mode [15]. This peak increased strongly as a function of the water content. When water is added, the dry α-D-glucopyranose should change into α-D-glucose monohydrate with C(6)H_2OH group changing from *gt* to *gg* [15]. Then the configuration of C(5)H-C(6)H_2 of α-D-glucose monohydrate [18] should be similar to that of β-D-glucopyranose [23]. Therefore, the increase of the peak at 2905 cm^{-1}as a function of the water content may be due to the rotation of C(6)H_2OH group from *gt* to *gg*. This is consistent with the Raman data with a very strong peak at 2907 cm^{-1} in the spectrum of β-D-glucose, but with a very weak peak in that of α-D-glucose [15].

The SFG peak at 2945 cm^{-1} should correspond to the Raman peak at 2942 cm^{-1} [15] for dry α-D-glucopyranose, while the SFG peak at 2935 cm^{-1} should correspond to the Raman peak at 2932 cm^{-1} [15] for wet α-D-glucopyranose. According to Ref. [15] they are attributed to the CH stretching vibration at C(1), C(4), and C(6).

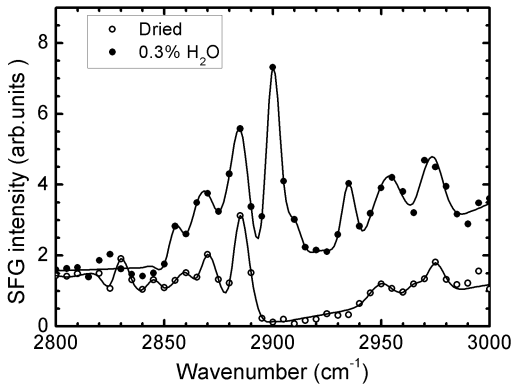

Figure 4: SFG spectra of D-glucose added with 0.3% H_2O (line with closed circle points) and after dried (line with opened circle points) for the polarization combination of SPP. Lines are multiple Gaussian functions fitted to the experiment.

Figure 4 shows SFG spectra of D-glucose containing 0.3% water (line with closed circle points) and the D-glucose after drying (line with open circle points). The SFG spectrum of the dried sample in Fig. 4 is quite similar to the spectrum of the dry α-D-glucose in Fig. 3. We see that the spectra can return to that of dry sample after drying from any initial percentage of the water content. Namely, the α-D-glucose monohydrate almost returned to α-D-glucose state after drying.

SFG spectra of α-D-glucose were once reported by Mizutani et al [20] and Miyauchi et al [6]. However, the water content of their samples were not specified. Judging from the present result, the sample analyzed in Ref. [20] had less water content than the one analyzed in Ref. [6].

Table 1. The assignment of the bands in CH region of vibrational spectra for dry and wet D-glucose.

Dry D-glucose (cm^{-1})		Assignment	Wet D-glucose (cm^{-1})	Assignment
SFG (this study)	Raman [15]		SFG (this study)	
2885	2880	ν(CH) at C(6)	2885	asymmetric C(6)-H-C(5)-H
2905	2912	ν(CH)	2900	symmetric C(6)-H-C(5)-H
2945	2942	ν(CH)	2935	ν(CH)
2955	2960	$\nu_a(CH_2)$	2955	$\nu_a(CH_2)$

ν(CH): CH stretching mode; $\nu_s(CH_2)$: symmetric CH_2 stretching mode; $\nu_a(CH_2)$: asymmetric CH_2 stretching mode

3.2. D-fructose

Figure 5 shows SFG spectra of dry D-fructose, i. e. β-D-fructopyranose, for four polarization combinations PPP, SPP, PSP and SSP. All the spectra have peaks at 2885 cm^{-1}, 2930 cm^{-1}, 2940 cm^{-1}, and 3010 cm^{-1}. There is some difference in the spectra among different polarization combinations. The peak at 2970 cm^{-1} is strong in the spectra for PPP and SPP but very weak in those for PSP and SSP. The peak at 2995 cm^{-1} is weak in the spectra of PPP and SPP but strong in

those for PSP and SSP. According to eq. (2), second-order nonlinear susceptibility depends both on Raman polarizability tensor elements and vibrational dipole moment [22]. In the four polarization configuration adopted in Fig. 5 the infrared light was always p-polarized. Thus the excited infrared dipole A_γ was in the same direction in the four measurements and it is different Raman polarizability elements $M_{\alpha\beta}$ that should be the reason for the different SFG intensity spectra. Hence we assume nearly one-to-one correspondence between the SFG and Raman spectra of D-fructose.

Table 2 lists the assignment of the peaks of the SFG spectra of D-fructose, based mainly on the assignment of the Raman data [24]. The SFG peak at 2885 cm^{-1} corresponds to the Raman peak at 2895 cm^{-1}, and is assigned to the $\nu_s(CH_2)$ mode. The SFG peak at 2930 cm^{-1} corresponds to the Raman peak at 2936 cm^{-1}, and is assigned to the mode $\nu_s(CH_2)$ at C(6) . The SFG peak at 2970 cm^{-1} corresponds to the Raman peak at 2956 cm^{-1} or 2962 cm^{-1} and is assigned to the ν(CH) mode. The SFG peak at 2995 cm^{-1} corresponds to the Raman peak at 2987 cm^{-1}, and is assigned to the $\nu_a(CH_2)$ mode at C(6). The SFG peak at 3010 cm^{-1} corresponds to the Raman peak at 3014 cm^{-1}, and is assigned to the $\nu_a(CH_2)$ mode.

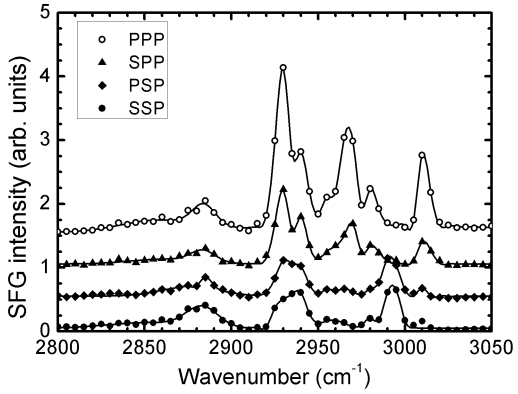

Figure 5: SFG spectra of dry D-fructose in four polarization combinations as PPP, SPP, PSP and SSP. Lines are multiple Gaussian functions fitted to the experiment. The zero levels of the spectra are displaced in the vertical direction for convenience to the eyes.

Table 2. The assignment of the bands in CH region of vibrational spectra for dry and wet D-fructose.

Dry D-fructose (cm^{-1})		Assignment [24]	Wet D-fructose (cm^{-1})	Assignment [24]
SFG (this study)	Raman [15]		SFG (this study)	
2885	2895	ν_s (CH_2)	2890	ν_s (CH_2)
2930	2936	ν_s (CH_2) at C(6)	2935	ν_s (CH_2)
2970	2962	ν(CH)	2970	ν(CH)
2995	2987	ν_a (CH_2) at C(6)	2990	ν_a(CH_2)
3010	3014	ν_a(CH_2)	3010	ν_a(CH_2)

ν(CH): CH stretching mode; ν_s(CH_2): symmetric CH_2 stretching mode; ν_a(CH_2): asymmetric CH_2 stretching mode.

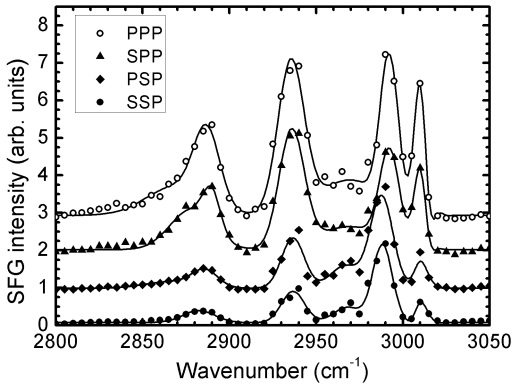

Figure 6: SFG spectra of wet D-fructose with 0.2% H_2O in four polarization combinations as PPP, SPP, PSP and SSP. Lines are multiple Gaussian functions fitted to the experiment. The zero levels of the spectra are displaced in the vertical direction for convenience to the eyes.

Figure 6 shows the SFG spectra of wet D-fructose with 0.2% H_2O content in four polarization combinations. The spectra for PSP and SSP combinations are similar to each other, and the spectra for PPP and SPP combinations have the same shapes. The spectra show a change from those of the dry sample in Fig. 5. The SFG spectra of the wet D-fructose did not depend on the percentage of the water content.

As mentioned earlier, D-fructose can dissolve in water and reaches the equilibrium state consisting of 60% β-D-fructopyranose, 30% α-D-fructofuranose, and 10% β-D-fructofuranose irrespective of the initial state [14]. We propose that the β-D-fructopyranose in the dry D-fructose transformed partially to furanose anomers when water is added to the sample. The main structural difference between pyranose and furanose anomers is at $C(6)H_2$ as shown in Figs. 1(c-f). The wet sample should thus contain two types of $C(6)H_2$. Accordingly, the peak at 2930 cm^{-1} assigned to ν_s ($C(6)H_2$) in the spectra of the dry sample is shifted and broadened at around 2935 cm^{-1}. The peak assigned to ν_a ($C(6)H_2$) in the spectra of the dry sample (at 2995 cm^{-1}) is broadened and shifted to 2990 cm^{-1}. Except for these detailed differences in the intensity and the line shapes, the SFG peaks of the dry D-fructose correspond to those of the wet one very well. Thus based on the assignment of the SFG spectra of the dry sample, the bands in the SFG spectra of the wet sample were also assigned in Table 2

3.3. Sucrose

Figure 7 shows the SFG spectra of dry sucrose for four polarization combinations PPP, SPP, PSP and SSP. All the four spectra in Fig. 7 are almost similar to each other. Although there exist infrared and stimulated Raman works of sucrose [8,25], there has been no vibrational mode assignment in the C-H stretching region.

As shown in Fig. 1(g), sucrose consists of α-D-glucopyranose and β-D-fructofuranose bonded by a glycosidic linkage. Thus the spectrum of dry sucrose should be a combination of the spectral features of α-D-glucopyranose and β-D-fructofuranose. So, in order to interpret the SFG spectra of sucrose, it would be useful if we have the SFG spectra of α-D-glucopyranose and β-D-fructofuranose. The SFG spectrum of α-D-glucopyranose with water content of 0% has been already shown in Fig. 3. On the other hand, in a stable state there is no crystalline powder of 100 % β-D-fructofuranose available. The SFG spectra reported in Section 3.2 is mainly of β-D-fructo*pyranose*. However, it is natural to infer that furanose anomers may have some contribution in the spectra of wet D-fructose in Fig. 6. Thus in the interpretation of the spectra of sucrose below, we consider the spectra of dry and wet D-fructose in Figs. 5 and 6 as a reference.

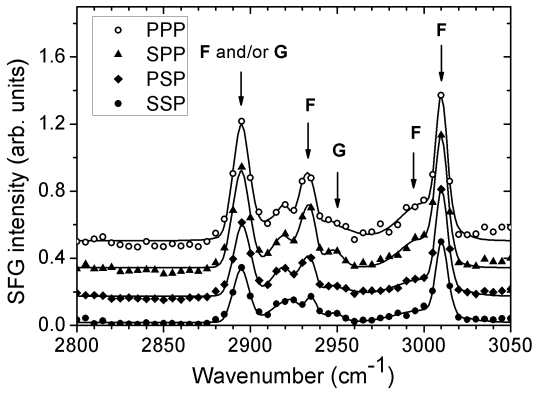

Figure 7: SFG spectra of dry sucrose in four polarization combinations of PPP, SPP, PSP and SSP. The letters F and G indicate that the peaks are attributed to β-D-fructofuranose and α-D-glucopyranose parts, respectively. Lines are multiple Gaussian functions fitted to the experiment. The zero levels of the spectra are displaced in the vertical direction for convenience to the eyes.

The detailed assignment of the spectra of dry sucrose is shown in Table 3. The peaks at 2935 cm^{-1}, 2990 cm^{-1} and 3010 cm^{-1}seen in Fig. 7 did not appear in the spectra of dry α-D-glucopyranose in Fig. 3 and so may be attributed to the β-D-fructofuranose part. Based on the assignments of bands for dry and wet D-fructose, we assign the peaks at 2935cm^{-1}, 2990 cm^{-1} and 3010 cm^{-1} in Fig. 7 to $\nu_s(CH_2)$, $\nu_a(CH_2)$, and $\nu_a(CH_2)$ of β-D-fructofuranose part, respectively. On the other hand, the peak at 2950 cm^{-1} may be contributed by α-D-glucopyranose part and should be assigned to $\nu_a(CH_2)$ of D-glucose. A very strong peak at 2885 cm^{-1} may be contributed by both glucose and fructose because it appeared in all the spectra of Figs. 3, 5 and 6. Thus it should be assigned to ν(CH) of glucose and/or $\nu_s(CH_2)$ of fructose parts. We could not assign the peaks at 2920 $cm^{-1}$and 2975 cm^{-1}. They did not appear in either spectrum of D-glucose or D-fructose.

Table 3. Tentative assignment of the bands in CH region of vibrational spectra for sucrose.

Dry sucrose (cm^{-1})		Assignment
SFG (this study)	Raman [26]	
2885	2885	ν(CH), ν_s (CH_2) G, F
2920	2925	-
2935	2940	ν_s (CH_2) F
2950	2960	ν_a (CH_2) G
2975	2985	-
2990	2995	ν_a (CH_2) F
3010	3005	ν_s (CH_2) F

ν(CH): CH stretching mode; $\nu_s(CH_2)$: symmetric CH_2 stretching mode; $\nu_a(CH_2)$: asymmetric CH_2 stretching mode.

We also carried out measurements on wet sucrose with various amount of water content less than 10%. The SFG spectra of the wet samples were similar to those of the dry sample at any percentage of the water content. At room temperature, sucrose in solution has been known to be stable. Hydrolysis does not occur to break the glycosidic linkage of sucrose. That is the reason why the spectral features of wet and dry sucrose are similar to each other.

4. CONCLUSION

SFG spectra of D-glucose, D-fructose and sucrose in four polarization combinations of incident visible, infrared, and SFG light fields in the C-H stretching vibrational regime were obtained. The wetting effect on the SFG spectra was investigated. The transformation of D-glucose from α-D-glucose to α-D-glucose monohydrate due to water effect was detected in the SFG spectra. The peak at 2900 cm^{-1} has been attributed to the α-D-glucose monohydrate. Change of β-D-fructopyranose form due to water effect was detected in the SFG spectra. The assignment of the SFG peaks of sucrose was performed by referring to the SFG spectra of D-glucose and D-fructose. The SFG spectra of sucrose did not change by wetting.

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