

OD bands in the IR spectra of a deuterated soda-lime-silica glass

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IR spectra of a deuterated glass of the composition (in mol%) $16 \text{ Na}_2\text{O} \cdot 10 \text{ CaO} \cdot 74 \text{ SiO}_2$ complete earlier spectroscopic studies on water-poor soda-lime-silica glasses. The approved IR spectroscopic method of the deuterium exchange allows a reliable assignment of the hydroxyl bands also in the case of glasses. By spectra comparison the assignment of the IR bands at 3500 and 2800 cm^{-1} to hydroxyl groups with different hydrogen bonding is verified. The IR band at about 4500 cm^{-1} is interpreted as both a combination of the stretching vibrations $\nu\text{O-H}$ and $\nu\text{Si-OH}$ and a combination of the stretching vibration $\nu\text{O-H}$ and the deformation vibration δSiOH . The bands at 1763 and 1602 cm^{-1} are attributed to combination vibrations of the glass network.

OD-Banden in den IR-Spektren eines deuterierten Kalk-Natron-Glases

Die IR-Spektren von einem mit D_2O bewässerten Glas der Zusammensetzung (in Mol-%) $16 \text{ Na}_2\text{O} \cdot 10 \text{ CaO} \cdot 74 \text{ SiO}_2$ vervollständigen frühere spektroskopische Untersuchungen an wasserarmen Kalk-Natron-Gläsern. Die in der IR-Spektroskopie bewährte Methode des Deuteriumaustausches führt auch im Falle der Gläser zu einer gesicherten Zuordnung der Banden der Hydroxylgruppen. Der Spektrenvergleich bestätigt die Zuordnung der IR-Banden bei 3500 und 2800 cm^{-1} zu Valenzschwingungen von Hydroxylgruppen mit unterschiedlich starken Wasserstoffbrückenbindungen. Die IR-Bande bei circa 4500 cm^{-1} wird sowohl dem Kombinationston der Valenzschwingungen $\nu\text{O-H}$ und $\nu\text{Si-OH}$ als auch dem Kombinationston der Valenzschwingung $\nu\text{O-H}$ und der Deformationsschwingung δSiOH zugeordnet. Die Banden bei 1763 und 1602 cm^{-1} sind Kombinationsschwingungen des Glasnetzwerkes.

1. Introduction

Numerous IR investigations on hydroxyl groups and water in glasses were published [1 to 15]. The subject has been studied systematically and extensively. Nevertheless, the assignments of the IR bands are contradictory in some studies. Most frequently the band assignment of Scholze [1 to 4] is used for water-poor silicate glasses. It should be mentioned however, that precise structures of water and hydroxyls in glasses can only be concluded from a proved interpretation of vibrational spectra.

Comparison of the spectra of hydrated and deuterated glass samples may be helpful for band assignments. Scholze and Franz [5] studied a deuterated glass of the composition (in mol%) $20 \text{ Na}_2\text{O} \cdot 30 \text{ CaO} \cdot 50 \text{ SiO}_2$ and demonstrated that all of the three OH stretching bands at 3550 , 2800 and 2350 cm^{-1} shift by a factor of nearly 1.37 to lower wave numbers due to deuterium exchange. The assignment of the 2350 cm^{-1} band as an OH stretching vibration was proved by this result. Uchino et al. [12] confirmed the interpretation by measuring the infrared spectra of thin films of hydrated and deuterated

sodium silicate glasses of the composition (in mol%) $30 \text{ Na}_2\text{O} \cdot 70 \text{ SiO}_2$ with a water content of more than 1 up to 38 wt% in the spectral region from 4300 to 400 cm^{-1} . The given interpretation differs from that of Scholze. Uchino et al. attributed the IR bands at 2800 and 2350 cm^{-1} to strongly hydrogen-bonded water molecules.

This work aims to analyse IR band shifts due to deuteration of a soda-lime-silica glass with the composition (in mol%) $16 \text{ Na}_2\text{O} \cdot 10 \text{ CaO} \cdot 74 \text{ SiO}_2$, which was studied in detail in previous papers [16 and 17], and to propose a band assignment. Raman spectra of the same samples were measured in order to check the network spectrum before and after hydration procedures.

2. Experimental

The preparation of the soda-lime-silica glass was described earlier as well as the hydration and drying procedures [16 and 17] (table 1). The raw materials used were dried sodium carbonate, calcium carbonate and quartz sand. The basic glass was molten in a platinum

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Table 1. Studied samples of the soda-lime-silica glasses; composition (in mol%): 16 Na₂O · 10 CaO · 74 SiO₂; thickness, *d* in mm; water concentration, *c* in mol · l⁻¹

glass no.	sample treatment	<i>d</i> in mm	<i>c</i> in mol · l ⁻¹
1	as-melted	0.12	0.019
2	as-melted	4.98	0.019
3	D ₂ O for 20 min	0.48	0.12
4	H ₂ O for 60 min	0.47	0.155
5	N ₂ dried 60 min	4.95	0.012
6	N ₂ dried 60 min	0.10	0.012

crucible in an induction furnace at 1500°C for nearly 16 h. The glass was homogenized by stirring the melt. Glasses of enriched water contents were obtained by re-melting a small part (50 g) of the base glass and by bubbling the melt with steam at 1450°C for 1 h. The deuterated glass was treated at the same temperature conditions, but the bubbling time was reduced to 20 min. The bubbling rate of liquid water was 0.5 ml · min⁻¹. Glass of reduced water content was prepared analogously using dried nitrogen as bubbling gas with a gas flow of 1 l · h⁻¹.

The water content of the studied glasses is also given in table 1. It was determined by nuclear reaction analysis for the samples nos. 1, 2, 4, 5 and 6. For the deuterated sample no. 3 the water content was estimated from the νOD band at 2595 cm⁻¹ using the practical extinction coefficient of the νOH band at about 3500 cm⁻¹.

For MIR and NIR transmission measurements the samples were prepared as plates of various thickness, from 0.10 to 5.00 mm (table 1). The plates were polished on both sides. Infrared absorption spectra were measured using a vacuum Fourier transform infrared spectrometer IFS 66v (Bruker, Karlsruhe (Germany)) in the region from 6000 to 1400 cm⁻¹, with a resolution of 2 or 4 cm⁻¹. All the IR spectra were related to 1 mm sample thickness. The reflection losses at the sample surfaces were eliminated by subtracting the absorbance values at 4250 cm⁻¹ from the MIR spectra and at 5000 cm⁻¹ from the NIR spectra, respectively.

Raman spectra were measured in right angle scattering. For this, two pairs of opposite faces of the samples were polished. The measurements were performed on a Dilor XY Raman spectrometer (Dilor, Bensheim (Germany)) equipped with an N₂-cooled CCD camera as a detector. The samples were excited by an Ar⁺ laser (75 mW at 514.5 nm). Spectra were accumulated for 150 s.

3. Results

The IR spectra of as-melted (glass no. 1), hydrated (glass no. 4) and deuterated (glass no. 3) glasses are compared

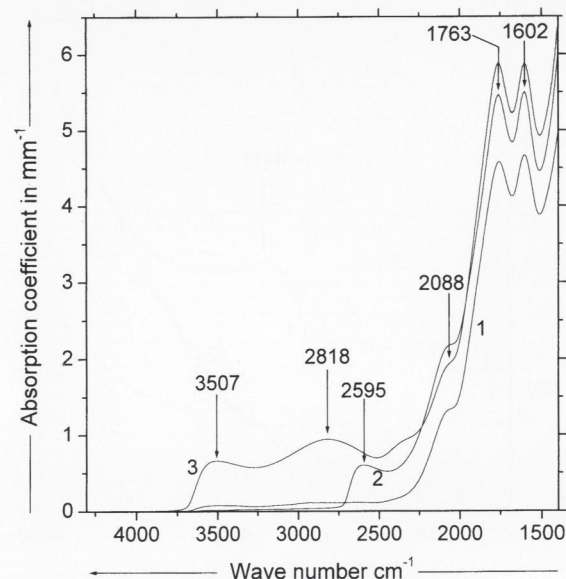


Figure 1. IR spectra of the glass 16 Na₂O · 10 CaO · 74 SiO₂; curve 1: glass no. 1, as-melted; curve 2: glass no. 3, deuterated for 20 min; curve 3: glass no. 4, hydrated for 60 min.

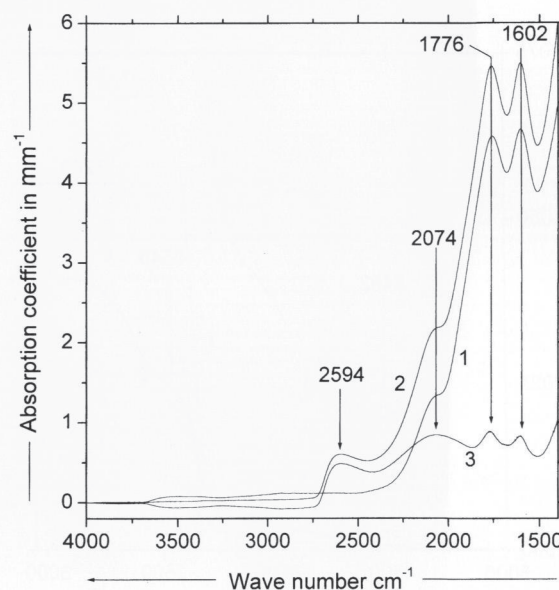


Figure 2. IR spectra of the glass 16 Na₂O · 10 CaO · 74 SiO₂; curve 1: glass no. 1, as-melted; curve 2: glass no. 3, deuterated for 20 min; curve 3: difference spectrum (glass no. 3 minus glass no. 1), obtained as difference between the spectra of the deuterated and the as-melted samples.

in figure 1. The OH band at about 3500 cm⁻¹ is shifted to 2595 cm⁻¹ due to deuteration. An OD band, corresponding to the OH band at about 2800 cm⁻¹, cannot be observed because of the strong network absorption below 2200 cm⁻¹. As can be seen from the difference spectrum (figure 2) the 2818 cm⁻¹ band shifts to 2074 cm⁻¹. In the difference spectrum the negative bands at about 3500 and 2900 cm⁻¹ show that the OH

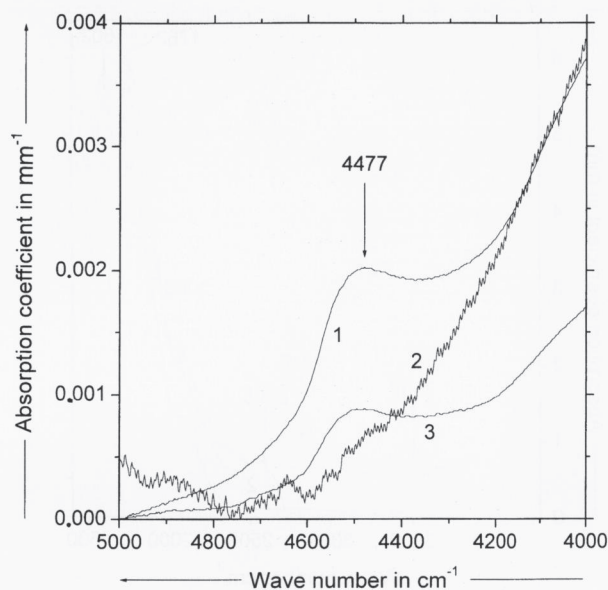


Figure 3. IR spectra of the glass $16 \text{ Na}_2\text{O} \cdot 10 \text{ CaO} \cdot 74 \text{ SiO}_2$; curve 1: glass no. 2, as-melted; curve 2: glass no. 3, deuterated for 20 min; curve 3: glass no. 5, N_2 dried for 60 min.

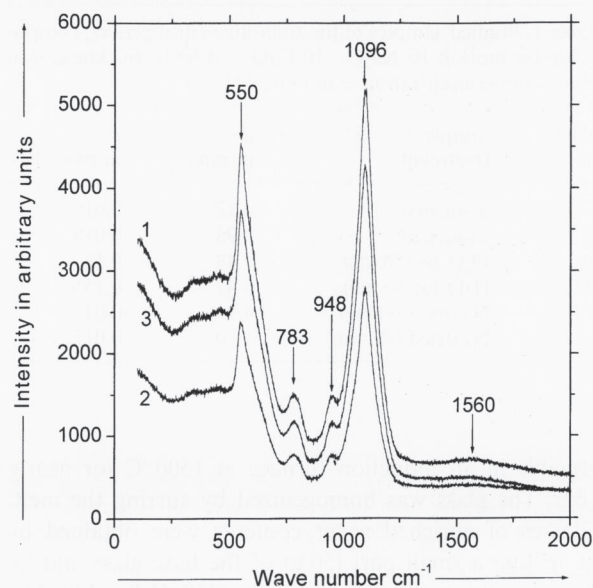


Figure 5. Raman spectra of the glass $16 \text{ Na}_2\text{O} \cdot 10 \text{ CaO} \cdot 74 \text{ SiO}_2$; curve 1: glass no. 2, as-melted; curve 2: glass no. 3, deuterated for 20 min.; curve 3: glass no. 4, hydrated for 60 min.

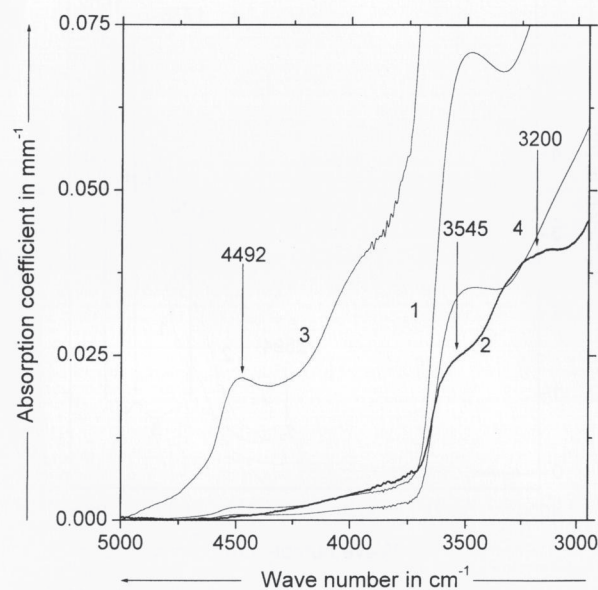


Figure 4. IR spectra of the glass $16 \text{ Na}_2\text{O} \cdot 10 \text{ CaO} \cdot 74 \text{ SiO}_2$; curve 1: glass no. 2, as-melted; curve 2 (dark line): glass no. 3, deuterated for 20 min; curve 3: glass no. 4, hydrated for 60 min; curve 4: glass no. 5, N_2 dried for 60 min.

groups in the as-melted sample are also deuterium exchanged. The 4500 cm^{-1} band disappears due to deuteration (figure 3). In the spectrum of the deuterated glass two weak and broad bands are observed at 3545 and 3200 cm^{-1} (figure 4). The spectra in figure 1 indicate that the bands at 1763 and 1602 cm^{-1} do not shift with deuterium exchange.

Nearly identical Raman spectra are obtained for all the studied samples, the as-melted glass (glass no. 2), and the glasses hydrated with H_2O or D_2O (glasses nos. 4 and 3) (figure 5). Thus, the glass network remains unchanged during hydration procedures.

4. Discussion

The assignment of the OH and OD bands in the infrared spectra is summarized in table 2.

The bands at 3507 and 2818 cm^{-1} in the spectra of the hydrated samples shift to 2595 and 2074 cm^{-1} , respectively, in the spectrum of the deuterated glass sample. The isotope ratio $\nu(\text{O}-\text{H})/\nu(\text{O}-\text{D})$ for these bands is 1.35 and 1.36, differing slightly from the corresponding harmonic value $\omega(\text{O}-\text{H})/\omega(\text{O}-\text{D}) = (\mu_{\text{OD}}/\mu_{\text{OH}})^{1/2} = 1.37$, where μ is the reduced mass. Thus, our findings agree with the result of Scholze and Franz [5].

In agreement with Wolters et al. [9], Uchino et al. [12] attributed the bands at 2800 and 2350 cm^{-1} to water molecules, hydrogen-bonded to nonbridging oxygen atoms in silicate glasses (table 2). In addition they found bands at 1760 and 1670 cm^{-1} and assigned these bands to bending vibrations of molecular water, strongly hydrogen-bonded and weakly bonded, respectively. The existence of strongly hydrogen-bonded water was supported by the appearance of the band at 1760 cm^{-1} . In our spectra the wave numbers of the bands are very similar to the experimental results reported in [12]. But in contrast to these we could not find an OH-related band at about 1760 cm^{-1} , which should be sensitive to deu-

Table 2. Assignment of IR bands of the water-poor soda-lime-silica glass in comparison with band assignment for the water-rich sodium silicate glass given by Uchino et al. [12]¹⁾; wave number, $\tilde{\nu}$

soda-lime-silica glass 16 Na ₂ O · 10 CaO · 74 SiO ₂ (in mol%)					sodium silicate glass 30 Na ₂ O · 70 SiO ₂ (in mol%)		
$\tilde{\nu}$ in cm ⁻¹					$\tilde{\nu}$ in cm ⁻¹		
deuterated glass no. 3	as-melted glass nos. 1, 2	hydrated glass no. 4	N ₂ dried glass nos. 5, 6	assignment	deuterated sample	hydrated sample	assignment ²⁾
	4477	4492	4492	$\nu\text{O}-\text{H} + \nu\text{Si}-\text{OH}$ and $\nu\text{O}-\text{H} + \delta\text{SiOH}$		4560	$\nu_{\text{A}}\text{H}_2\text{O}(\text{II}) + \delta\text{H}_2\text{O}(\text{II})$ and
						4540	$\nu_{\text{B}}\text{H}_2\text{O}(\text{II}) + \delta\text{H}_2\text{O}(\text{II})$ + $\text{RH}_2\text{O}(\text{II}) - \text{TH}_2\text{O}(\text{II})$
3545 3200				$\nu\text{O}-\text{D} + \nu\text{Si}-\text{OD}$ $\nu\text{O}-\text{D} + \delta\text{SiOD}$			
	3490	3507	3490	$\nu\text{O}-\text{H}$ } weak hydrogen $\nu\text{O}-\text{D}$ } bond	2630	3600	$\nu\text{O}-\text{H}$ $\nu\text{O}-\text{D}$
2595							
	2710	2818	2850	$\nu\text{O}-\text{H}$ } strong hydrogen $\nu\text{O}-\text{D}$ } bond	2170	2800	$\nu_{\text{A}}\text{H}_2\text{O}(\text{II})$ $\nu_{\text{A}}\text{D}_2\text{O}(\text{II})$
2074 ³⁾							
		2357 sh	2362 sh	$\nu\text{O}-\text{H}$, very strong hydrogen bond	1730	2350	$\nu_{\text{B}}\text{H}_2\text{O}(\text{II})$ $\nu_{\text{B}}\text{D}_2\text{O}(\text{II})$
2084	2075	2088	2080	network		2200	combination H ₂ O(I)
1763	1762	1765	1759	network		1760	$\delta\text{H}_2\text{O}(\text{II})$
						1670	$\delta\text{H}_2\text{O}(\text{I})$ $\delta\text{D}_2\text{O}(\text{I})$
					1230		
1602	1600	1603	1604	network			

¹⁾ From [12] the table contains only some bands of interest. Uchino et al. published a complete interpretation of the vibrational spectrum of the glass, including also network bands.

²⁾ (I) = water molecule interacting with a SiOH group or a SiOSi bridge; (II) = water molecule interacting with a nonbonding oxygen atom; A and B = two vibrational modes. R = hindered rotation; T = translation.

³⁾ From the difference spectrum in figure 2.

terium exchange. That is why we exclude molecular water in our case. Thus, there is no reason for revising Scholze's assignment for the 3500 and 2800 cm⁻¹ bands for water-poor glasses. But it can be concluded that the 2800 cm⁻¹ band is overlapped by one of the $\nu\text{H}_2\text{O}$ bands of the strongly hydrogen-bonded water at 2800 cm⁻¹ in the case of water-rich glasses. Uchino et al. [12] attributed the band at about 3600 cm⁻¹ to SiO-H stretching vibrations of the hydroxyl groups, formed as a result of the equilibrium between molecular water and hydroxyl groups, proposed by Stolper [10].

Assuming that no OH groups remain after deuteration, the bands at 3545 and 3200 cm⁻¹ can be attributed to the shifted OH band at 4492 cm⁻¹, which splits into two components. On the one hand, the combination band of the two stretching vibrations $\nu\text{O}-\text{H}$ and $\nu\text{Si}-\text{OH}$ of a silanol group should shift about 912 cm⁻¹ to lower wave numbers because of the deuterium shift of the $\nu\text{O}-\text{H}$ vibration. The wave numbers of the stretching vibration $\nu\text{Si}-\text{OH}$ and $\nu\text{Si}-\text{OD}$ should be nearly the same. Thus, the wave number of the combination band can be estimated to be 3580 cm⁻¹. It well agrees

with the observed band at 3545 cm⁻¹. On the other hand, the band of the deformation vibration δSiOH should be significantly shifted after deuteration. Both the fundamental vibrations $\nu\text{Si}-\text{OH}(\text{D})$ and $\delta\text{SiOH}(\text{D})$ cannot be observed in the IR transmission spectra because of the strong network bands. But the wave number of the band, corresponding to the 4492 cm⁻¹ band, can be estimated to be 3327 cm⁻¹, assuming an isotope ratio $\delta\text{SiOH}/\delta\text{SiOD}$ of 1.35. A weak and broad band at about 3200 cm⁻¹ is observed in the spectrum of the deuterated sample.

Three bands are recorded in the spectral region between 2200 and 1400 cm⁻¹ (figure 1). The wave numbers of these bands are the same for all the studied glass samples, i.e. about 2080, 1763 and 1602 cm⁻¹. No deuterium sensitivity was found for these bands. This behaviour suggests that hydrogen does not participate in these vibrations, therefore, these bands belong to glass network vibrations. In particular, this assignment is in contradiction to the interpretation published by Uchino et al. [12] (table 2) and also to the interpretation recently reported by Efimov et al. [15]. In this report bands at

about 2100, 1740 and 1590 cm^{-1} were attributed to stretching vibrations $\nu\text{O-H}$ of hydroxyl groups, participating in hydrogen bonding. Our findings are in contrast to such an interpretation. But it should be noticed that band absorbance in this spectral region increases with growing water content of samples regardless of whether the samples are hydrated or deuterated (see figures 1 and 2). These findings remain to be explained.

Hence, it is demonstrated that deuterium exchange is a powerful tool also for IR studies of hydroxyls and water in glasses. It provides a more complete base for band assignment, but further studies are needed to confirm the proposed interpretation.

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