Is adsorbed water responsible for 2800-3000 cm\(^{-1}\) band in Raman spectrum of inorganic matter?

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Abstract. In papers devoted to Raman spectra of SiO\(_2\)-(H\(_2\)O)\(_x\) gel, stishovite, silver surface and gold particles on copper surface the band at 2800 – 3000 cm\(^{-1}\) was attributed to adsorbed water in spite of the essential shift of this band relatively to conventional water band at \(\sim 3500\) cm\(^{-1}\). This interpretation is controversial and it needs to be discussed. Measurements of Raman spectra of a glass slide with a fingerprint allowed another interpretation of this band because deposition of the fingerprint on the slide surface resulted in appearance of 2800 – 3000 cm\(^{-1}\) Raman band, and Raman mapping of the slide surface reproduced a microphotograph of the fingerprint. This allows relating of this band to traces of organic compounds at the surface of the studied samples.

1. Introduction

Raman scattering technique is in use for materials characterization [1], sensing [2] and optical amplification [3]. It also has a high potential for studies of media containing dielectric [4], metal [5] or semiconductor nanoparticles [6], the latter being a perspective material for solid state lasers mode-locking [7]. It is essential that the locality of Raman technique in microRaman configuration is limited by the size of a microobjective focal spot only. This makes Raman technique attractive to characterize spatially non-uniform structures, e.g. formed using diffusion [8], laser irradiation [9] or other local techniques, like electric-field imprinting [10]. In all these cases exact attributing of Raman bands is crucial both for identification of media and following their behavior under different treatments. In particular, this relates to Raman bands in the region \(\sim 3000\) cm\(^{-1}\) [11].

There were at least three studies [12–14] where the Raman band at 2800 – 3000 cm\(^{-1}\) was associated with adsorbed water in spite of the essential shift of this band relatively to conventional water band at \(\sim 3500\) cm\(^{-1}\), and a special term “the giant shift” was introduced for this phenomenon. Different materials, namely SiO\(_2\)-(H\(_2\)O)\(_x\) gel [12], water-rich stishovite [13], water on silver surface and gold particles on copper surface [14], were the subjects of those studies. Nevertheless, the bands reported in Refs 12-14 have the same spectral position and very similar structure consisting of several lines. Contrary, the studies of adsorbed water at the surface (isolated, geminal, vicinal groups, chains OH, adsorbed water) and in the bulk of silica [15, 16], and at the surface of silver [17, 18] shows no bands in 2800 – 3000 cm\(^{-1}\) region. Besides, the authors of [14] mentioned that the spectra registered in their experiments were close to spectra of some biological objects they observed earlier. This allows
supposing that the band 2800 – 3000 cm\(^{-1}\) can indicate organic impurities at the surface of the samples. As known, organic molecules can contain functional groups CH (methane group), CH\(_2\) (methylene group) and CH\(_3\) (methyl group). These groups demonstrate characteristic vibrations of C-H bonds in the region of 2800 – 3000 cm\(^{-1}\) (stretching vibrations) and in the region of 1400 – 1500 cm\(^{-1}\) (bending vibrations) [19–21]. Thus to identify the 2800 – 3000 cm\(^{-1}\) band it is desirable to put attention to the region of 1400 – 1500 cm\(^{-1}\). However this region had not been studied in [13, 14], and the authors of Ref. 12 neglected it in spite of the presence of both, 2800–3000 cm\(^{-1}\) and 1400 – 1500 cm\(^{-1}\), bands in the spectra presented in their paper in figure 2(a, b) (573 K graph). Thus, the authors of Ref.12-14 did not provide enough arguments to relate the 2800–3000 cm\(^{-1}\) band to the band of adsorbed water.

2. Experiments and discussion

To illustrate possible origin of 2800 – 3000 cm\(^{-1}\) band an experiment with a fingerprint at the surface of a soda-lime glass (Menzel microscope slide purchased from Agar Scientific) has been performed. The fingerprint is chosen because it (like the oil of vacuum pumps and hydrocarbons) is a potential source of organic contamination of specimens and lab equipment.

![Figure 1](https://via.placeholder.com/150)

**Figure 1.** The band observed in Raman spectra of a glass slide with a fingerprint, which coincides with «adsorbed water» [12-14] band at 2800 – 3000 cm\(^{-1}\). Comparison of Raman spectra of the glass before (lower curve) and after (upper curve) leaving the fingerprint demonstrates the responsibility of the fingerprint for the appearance of 2800 – 3000 cm\(^{-1}\) band (C-H bonds stretching vibrations), and a set of peaks in 1400 – 1500 cm\(^{-1}\) region (C-H bonds bending vibrations) (a). The detailed spectrum of the glass with the fingerprint in 2800–3000 cm\(^{-1}\) region (b). The horizontal lines correspond to the interval of vibration frequencies.

Using Witec Alpha 300R Raman spectrometer equipped with a confocal microscope (WITec Wissenschaftliche Instrumente und Technologie GmbH, Ulm, Germany) has allowed 3D mapping of samples with 0.5 μm lateral resolution. Raman scattering was excited with 532 nm CW laser and 100x/0.9 microobjective. Morphology of the surface was characterized with optical profiler Zygo NewView 6000 (Zygo Corporation, Middlefield, USA). Overview Raman spectra of the slide surface
with and without the fingerprint are presented in figure 1(a), and the detailed spectrum in 2650 – 3250 cm\(^{-1}\) region is in figure 1(b). The spectral positions of stretching CH\(_3\) and CH\(_2\) vibrations for aliphatic compounds are marked in figure 1(b) for comparison. These are 2840 – 2870 cm\(^{-1}\) – symmetric vibrations of CH\(_2\) groups (\(\nu_s\) (CH\(_2\))), 2865 – 2885 cm\(^{-1}\) – symmetric vibrations of CH\(_3\) groups (\(\nu_s\) (CH\(_3\))), 2915 – 2940 cm\(^{-1}\) – asymmetric vibrations of CH\(_2\) groups (\(\nu_{as}\) (CH\(_2\))), 2950 – 2975 cm\(^{-1}\) – asymmetric vibrations of CH\(_3\) groups (\(\nu_{as}\) (CH\(_3\))) [19].

As it is seen from figure 1(a), the intensity of the Raman spectrum of the fingerprint in 2800 – 3000 cm\(^{-1}\) region is comparable with the intensity of the glass Raman spectrum. The main contribution in the Raman spectrum of fingerprint presented on figure 1(a, b), is one of saturated and unsaturated fatty acids mix (see [22] for comparison). Cleaning of the specimen in an ultrasonic bath with acetone during 1 min has resulted in decreasing intensity of 2800 – 3000 cm\(^{-1}\) band in the Raman spectrum by about an order of magnitude, nevertheless the band stays well detected (not shown in figure 1(a)). Structure of the band 2800 – 3000 cm\(^{-1}\) (see figure 1(b)) repeats with minor differences the band structure presented in Refs 12-14 (compare with figure 5 from [12], figure 4 from [13] and figures 1-2 from [14]). These differences are probably related with differences in the content of CH, CH\(_2\) and CH\(_3\) groups and in the character of bonds (saturated or unsaturated) in different organic compounds.

![Figure 2.](image)

Figure 2. Raman mapping of the fingerprint confirming the origin of the 2800 – 3000 cm\(^{-1}\) band. Microphotograph of the glass surface with the fingerprint (a) and the map of 2800 – 3000 cm\(^{-1}\) Raman band intensity in the marked region (60*60 points, objective 50x/0.8, the color bar indicates CCD counts) (b); 3D relief map of the part of the glass surface between two grooves of the fingerprint showing the height of the fingerprint-related contaminations, which varied from hundreds of nanometers up to 1 – 2 microns (c).

Optical image of a part of the slide surface with the fingerprint is demonstrated in figure 2(a), and the intensity map of 2800 – 3000 cm\(^{-1}\) Raman line in the region marked in figure 2(a) is shown in figure 2(b). Figure 2(c) shows a typical 3D relief map of the slide surface in the fingerprint region. Figure 2 proves that the Raman signal at 2800 – 3000 cm\(^{-1}\) measured in this experiment is related with the fingerprint. Importantly, the surface mapping is useful to identify traces of impurities because their surface distribution can be non-uniform. Figure 2(c) shows that two scales of the fingerprint
structure exist: i) the distance between the grooves and their width (see figure 2(a)) that is the major structure and ii) the fine structure consisting of lumps of various heights and diameters. Their average height is about hundreds of nanometers, but lumps up to 1–2 microns in height can be found.

It is worth to note that water is a bad scatterer in comparison to organics due to significantly lower polarizability of water molecules [23, 24]. Because of this, possible contribution of organic contaminations in Raman spectra can essentially exceed one of absorbed water if the latter is characterized using confocal microRaman technique.

3. Conclusions
This example shows that even relatively small, up to hundreds of nanometers, lumps of organic impurities can generate Raman signal comparable in intensity with a useful signal from the inorganic matrix under study and, thus, influence interpretation of experimental results. Finally, the identification of 2800–3000 cm$^{-1}$ band as one related to adsorbed water in Refs 12-14 is not obvious.

It should be emphasized that organic contaminations can be a serious problem in using high sensitive Raman spectroscopy techniques, like Surface Enhanced or Tip Enhanced Raman Scattering, and a rigorous analysis with the use of corresponding databases (see, e.g. [19, 20] and references therein) excluding the presence of organic impurities in inorganic samples under study is desirable for precise identification of Raman bands.

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