

Intensity redistribution of bending and stretching Raman scattering bands in water upon degassing and crystallisation

S.M. Pershin, A.F. Bunkin, S.D. Zakharov, V.A. Luk'yanchenko

Abstract. It is established for the first time that the intensities of bending and stretching Raman scattering (RS) bands in water vary oppositely in the processes of degassing and crystallising. Water degassing shifts the centre of a stretching OH band to higher frequencies by approximately 2 cm^{-1} , which points to a reduced contribution of structural complexes to the RS spectrum.

Keywords: Raman scattering spectroscopy in water, amplitude ratio for bending/stretching vibrations in H_2O degassing/crystallising.

It is known [1–5] that removal of dissolved atmospheric gases from water (degassing) is accompanied by change in its physical properties. Vallee et al. [2] found a fall of the amplitude of elastic scattering at the probe signal wavelength (488 nm), which points to a reduced water heterogeneity and smaller contribution of structural complexes into the molecular scattering. Removal of air [3] was accompanied by an elevated ($\sim 30\%$) water electrical conduction and dissolving capability (a change in the surface free energy or wettability), which was revealed in the origin of highly dispersed emulsion with oils under shaking. A higher threshold of optical breakdown in degassed water [4] is also explained by an increasing optical homogeneity due to a breakdown of gas-hydrate complexes. Recently [5], the hypothesis on existence of a water structure [1] in the form of ice-like (hexamer) and disordered complexes was confirmed by the small-angle X-ray scattering method.

The authors of [6, 7] succeeded in revealing a specific role, which oxygen plays in variations of water physical properties. Water degassing resulted in a reduced susceptibility to a magnetic field action, which was observed as a reduction of surface tension (the angle of drop wettability). It was found that only saturation of water by oxygen (oxygenation) recovers the susceptibility. Simultaneous deformation of the stretching OH band was observed in

IR absorption [6] and Raman scattering (RS) [7] spectra. The deformation is usually explained by the contributions from ordered and amorphous forms of hydrogen-bond complexes [8].

In analysing the IR water spectra from [6] (see Fig. 1) we noticed the reduction of the amplitude ratio for the bending and stretching vibrations in H_2O molecule after oxygenation of degassed water, which was not discussed in the work. Earlier [9], in studying the light-oxygen effect in water and aqueous erythrocyte suspensions we have found that the presence of oxygen is accompanied by a reduction of the refractive index of a liquid. This was explained by a greater part of hydrogen-bond ice-like complexes and we assumed that the lower amplitude of bending relative to stretching vibrations [6] in oxygenising degassed water may point to a greater part of the ice-like complexes.

The aim of the present study is an experimental verification of this assumption by the RS method in water after degassing and crystallising it when the structure character dominates. Evolution of the envelope for a stretching RS band was quantitatively estimated (which has not been done in [6]) by the shift of the band centre. The information importance of this approach was substantiated in our earlier works [10, 11].

The experiment was performed on an RS spectrometer by the backscattering scheme [10] with second-harmonic pulses (532 nm) of a Nd:YAG-laser operating at the pulse repetition rate of 2 Hz. The pulsed laser was needed to reduce an average radiation power and duration of its action on water, because in a cw laser these factors result in an additional bending of RS bands [12]. The laser radiation was focused to a quartz cell filled with water ($50 \times 30 \times 20$ mm) or to a transparent ice sample ($30 \times 25 \times 18$ mm) by a lens with a focus of 7 cm. The lens focused the RS radiation which was directed to a polychromator by a folding mirror. The backscattered radiation of a laser was attenuated by an OS-13 light filter. The second-harmonic pulse energy was $300\text{ }\mu\text{J}$. The RS spectrum was detected with a diode array (Andor iStar) cooled to -20°C with the light amplifier placed in front of it, which was gated by 30-ns pulses. After averaging over 300 pulses, the spectra obtained were recorded and analysed. The wavelength scale of the polychromator with a grating of 150 lines mm^{-1} was calibrated in the range 500–700 nm by neon lines in a gas discharge. The spectral resolution was 0.7 nm (approximately 8 cm^{-1}). After recording the RS spectrum, a noise of the array is also recorded with the same accumulation cycle and closed laser beam with the following subtraction of the noise spectrum from RS spectrum in water and ice.

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Distilled water was used as an initial sample, which was then degassed via boiling for 15 minutes in a Pyrex glass. Then the water was poured to a glass container, tightly closed and the remaining air was repeatedly pumped out to the pressure of saturated vapour as water gradually cooled. All the measurements were taken at a temperature of 22 °C. Ice samples were prepared from degassed water by slowly cooling it in a container (30 × 25 × 18 mm) from polyethylene at the temperature of a cooling chamber base -10 °C. Among several ice samples, one was chosen with a transparent domain along the longer side. Taking into account that the rate of atmospheric gas diffusion into degassed water under normal conditions [3] is ~14 mm hour⁻¹, we filled the cell just before starting the measurements. The laser beam propagated at a depth of 25 mm under the water surface, which provided recording RS spectra for 1–2 hours without increasing the concentration of dissolved gases. The degree of water degassing during boiling was determined by measuring the oxygen concentration with the Clark electrode (Expert-001, Econix, Russia). After boiling, the initial oxygen concentration [280 μM (1.7 × 10¹⁷ mL⁻¹)] reduces to 50 μM.

In Fig. 1, three RS spectra are shown in the frequency shift band 900–4000 cm⁻¹ in distilled and degassed water along with an ice spectrum. Since the water spectra were measured under similar conditions, for convenience of comparison we normalised them (after subtracting the noise) to the amplitude of stretching vibrations (3450 cm⁻¹). Insertion in Fig. 1 presents these spectra in a larger scale near the frequencies of bending (~1630 cm⁻¹) and combined (~2130 cm⁻¹) vibrations. To compare the amplitudes in this spectral range, the spectrum of ice was multiplied by the factor providing the amplitude of ice spectrum comparable with a minimal amplitude of water spectra at the frequencies 900, 1800, and 2300 cm⁻¹, which fit the wings of the bands 1630 and 2130 cm⁻¹.

In Fig. 1 one can see that water crystallisation results in a substantial amplitude fall of the bending vibrations. This fact agrees with the reduction of the amplitudes of these

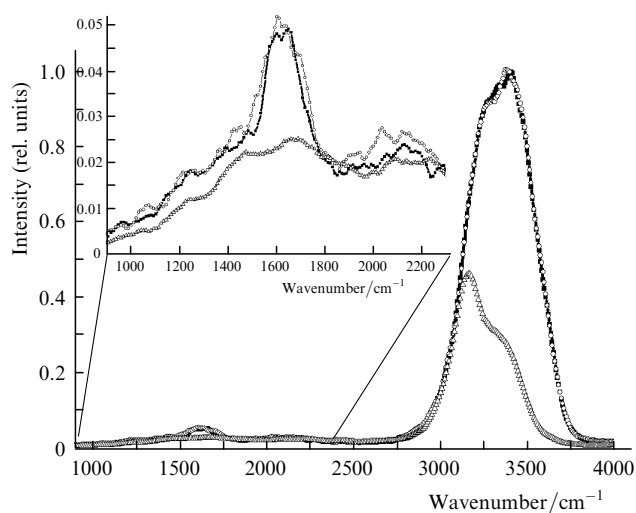


Figure 1. Raman scattering spectra of distilled (■) and degassed (○) water, and ice (△) [6]. Inset: an enlarged fragment of the RS spectrum in the vicinity of a bending vibration band. The experimental error calculated by five measurements is ~4% near the frequency of 1600 cm⁻¹.

vibrations in oxygenation of degassed water observed in [6]. Seemingly, it is related to a limited amplitude of bendings of the H₂O molecule imbedded into a crystal lattice of hexagonal ice. In contrast, water degassing is accompanied by an increased amplitude of bending and combined vibrations as compared to stretching vibrations.

In this case, the centre of a stretching vibration band measured by the centre of the Gaussian envelope of an OH contour, which approximates the experimental contour by the least-squares method used in [10, 11] is shifted by 2 cm⁻¹ to the high-frequency wing of degassed water as compared to distilled. Usually such a shift is explained by a bending of the OH band in heating [10, 13]. An analysis of the OH band based on its approximation by several Gaussian contours [12, 14, 15] or on the ratio of amplitudes of low- and high-frequency wings of the band [16] also allows one to speculate about band bending. Obviously, at greater number *n* of approximating contours (and the corresponding parameters, 3*n*), the dependence of the parameters on each other, on the initial conditions of a nonlinear regression, and on participation of an experimenter in the approximation process is stronger. Conversely, the single-contour approximation substantially simplifies establishing the fact of OH-band bending and provides a quantitative criterion for the shift of its centre [10, 11]. A physical meaning of the shift of the OH-band centre was discussed earlier in our studies [17, 18].

Thus, the experimental data prove that water degassing and crystallisation are oppositely revealed in a change of the amplitude of bending (1630 cm⁻¹) vibrations in the H₂O molecule. A reduction of bending vibration amplitude in dissolving atmospheric gases in water may be explained by a growing part of gas-hydrate structure complexes which disintegrate under degassing. A comparison with the results [6] shows that, seemingly, oxygen makes the main contribution into such processes. It is reasonable to assume that more intense degassing of water and saturation it with oxygen will enhance the contrast of the effect observed by using the bending vibration band as an indicator of the degree of water structuring and oxygenation.

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