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From clusters to condensed phase – FT IR studies of water

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ABSTRACT

Intermolecular hydrogen bonding, which is formed between water molecules in the condensed state, causes a variety of unique properties of liquid water. In this paper the results of experimental FT IR studies of water trapped in an Ar matrix as well as condensed water at temperatures from 133 to 293 K are presented. It is shown that the temperature evolution of the FTIR-spectra of water trapped in low-temperature matrices can be considered as an experimental model of the structure transformation of water during the phase transition from gas phase to condensed confined water. The comparison of the vibrational spectra of water in matrix isolation with the corresponding spectra of condensed water gives information about the peculiarities of H-bonded structures of water.

1. Introduction

Water is the most important liquid on our planet and it is also one of the most anomalous with many properties that deviate from those of other liquids [1], so it is not surprising that it has been intensively studied by various methods. In recent years, several reviews have been devoted to different aspects of water [2–6] devoted to experimental and theoretical investigations of water structure and properties. Of particular interest in connection with the present work is the large number of experimental studies using infrared spectroscopy and matrix isolation techniques to determine properties of small aggregates of water molecules [7–19], Intermolecular hydrogen bonding, which is formed between water molecules, causes a variety of unique properties of this liquid. These anomalous properties of water were studied both by experimental and theoretical methods [3,20,21].

Among spectroscopic investigations of water structure, the work of Tukhvatullin et al. [22] should be mentioned, where the polarized components of Raman spectra of O—H vibrations in liquid water were investigated. It was shown that the experimentally observed broad band in the region 3000–3800 cm^{-1} in Raman spectra of liquid water can be viewed as a superposition of two systems of bands with different magnitudes of the depolarization ratio. One system of bands was proposed to be associated with the symmetric (low-frequency) O—H vibration of the water molecule. The other system of vibrational bands was proposed to be associated with the “antisymmetric” (high-frequency) vibration. This assignment was supported by quantum-chemical calculations on cluster models of local water structures [22], which show a red shift of the symmetric and antisymmetric vibrations with increasing number of molecules in the clusters. Moreover, the distance between them increases from 100 cm^{-1} for the monomer to 200 cm^{-1} for the pentamer. Thus, having compared the experimental spectra of liquid water with results of calculations for various size cluster models the authors of [22] suggested the presence of aggregations consisting of at least five molecules in liquid water. Indeed, pentamers as the dominating smallest closed H-bond loop has been suggested for supercooled water by Russo et al. [23], but not as clusters but rather as topological features of the H-bonding network. This has recently been supported by Martelli et al. [24] based on analysis of *ab initio* molecular dynamics trajectories.

An alternative interpretation of the two dominating bands in the liquid Raman spectrum and their dependence on temperature and salt concentration [25,26] is in terms of two predominant local H-bonding structures, respectively high- (HDL) and low-density liquid-like (LDL) reminiscent of the well-established HDA and LDA forms of the amorphous ices [3]. This interpretation is directly related to scenarios to explain the origin of the apparent divergence of response functions [27,28] and is furthermore supported by interpretations of x-ray spectroscopic data [3,29–31] although this is not without controversy [32–35].

To distinguish between spectral bands, which belong to clusters of a certain size, methods of their isolation in low-temperature matrices are often used [11–17,36–39]. As was shown in [40–42], the heating of hydrogen-bonded liquids trapped in low-temperature matrices allows tracing the transformation of their cluster structure from monomers

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and dimers to larger molecular clusters. Such experiments may be considered as a model of a phase transition from gas consisting of individual molecules to the condensed state with its H-bonded structure. The aim of the present work is to analyze the temperature evolution of the registered FTIR spectra of water trapped in Ar matrices to assign the observed bands to clusters of different size and to explore how these results can be used to explain the temperature changes observed in vibrational spectra of water in the condensed state.

2. Experimental

All experiments, which are presented in this work, were carried out in the Fourier transform vibrational spectroscopy laboratory at the Physics Faculty of Vilnius University, Lithuania.

Liquid deionized and triple-distilled water was used in the experimental spectroscopic investigations. The sample was cooled to 133 K and then gradually heated to 293 K with simultaneous registration of spectra. The gaseous water sample was obtained by natural evaporation from the liquid and subsequently mixed with argon (purity - 99.995%) in the approximate ratio 1:1000, as measured by standard manometric techniques. The obtained mixture was deposited at 9 K onto a CsI window during 1 h. The deposition rate was 5 mmol of matrix mixture per hour. Then FTIR absorption spectra were measured at temperatures from 9 to 50 K using an IFS 113 FTIR spectrometer from Bruker. A liquid-N_2-cooled mercury cadmium telluride (MCT) detector was used. Thermostabilization was provided by a closed-cycle Leybold Heraeus RW2 He cryostat and the temperature was controlled with a Si diode sensor and Lakeshore temperature controller with accuracy 0.1 K. Spectra were recorded in the spectral range from 500 to 4000 cm^{-1} with optical resolution 0.5 cm^{-1}. In order to increase the signal-to-noise ratio each spectrum was taken as an average of 512 scans.

Infrared absorption spectra of condensed water were recorded using Bruker's FTIR spectrometer VERTEX 70 with spectral resolution 1 cm^{-1}. Raman spectra were recorded using an FT-Raman MultiRam Bruker spectrometer with a 785 nm laser (500 mW) and a Silicone Avalanche diode as detector. Thermostabilization during temperature investigations in the condensed states was provided by a LINKAM cryostat (model FTIR 600). FTIR spectra of the condensed phase were recorded in the spectral range from 500 to 4000 cm^{-1} and in the temperature range from 133 to 353 K at increments of 2 K.

3. Results and discussion

It is well known that vibrational spectra of the water molecule consist of only three vibrational bands: one near 1600 cm^{-1} corresponding to the bending O—H vibration and two in the region 3650–3750 cm^{-1} corresponding to the symmetric and asymmetric stretching vibrations. However, intermolecular H-bonds between water molecules cause the appearance of additional low-frequency bands in vibrational spectra of water, which are assigned to intermolecular vibrations [16,17]. The registered FTIR spectra of water trapped in an Ar matrix at temperatures from 9 K to 50 K are presented in Fig. 1.

Increasing the matrix temperature changes the conditions for the formation of water clusters. When the matrix is heated, the possibility to form bigger clusters appears. Thus, one can observe the temperature evolution of the registered spectra with new vibrations appearing in the spectral region 500–1200 cm^{-1} as the result of hydrogen bonding between water molecules. These bands correspond to intermolecular vibrations. Their maximum positions depend on the matrix temperature. The group of bands in the region 1550–1750 cm^{-1} is derived from the molecular bending O—H vibrations, while the system of bands in the region 3000–3800 cm^{-1} derives from the stretching symmetric and asymmetric vibrations. The temperature evolution of these spectra is caused by diffusion in the isolating matrix structure, which allows the formation of bigger clusters of water at higher temperatures. It should be noted that the spectrum at 9 K is very similar to the spectrum of gas phase (without rotational structure), *i.e.* derived from isolated molecules in the matrix, and at 50 K (when argon has evaporated) it looks like the spectrum of the condensed phase.

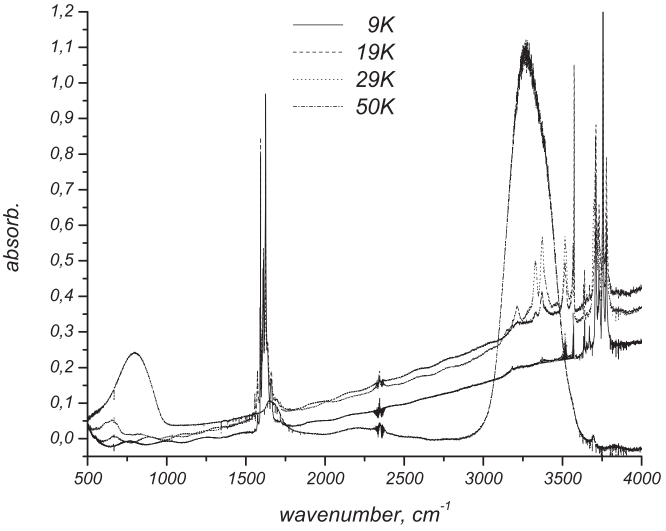

Fig. 1. FTIR spectra of water trapped in an Ar matrix at different temperatures.

The low-frequency part of the registered spectra (500–1500 cm^{-1}) is presented in Fig. 2. It is seen that these spectra transform with increasing temperature. The authors of [16] assign the bands at 655 cm^{-1} and at 679 cm^{-1} to out-of-plane bending vibrations in water tetramers At 29 K clusters of both smaller (613 cm^{-1}) and bigger (830 cm^{-1}) sizes appear. When the matrix temperature reaches 50 K, one can observe the band at 800 cm^{-1}, which is very similar to that registered in condensed phase. This fact allows concluding that the temperature evolution of IR spectra of water in matrix isolation is an experimental model of phase transition gas – condensed water.

The temperature evolution of the FTIR spectra of water trapped in an Ar matrix in the spectral region of bending vibrations is presented in Fig. 3. The complex structure of this band can be explained by the simultaneous existence of different water clusters. The bands, which are the most intense at the lowest temperature – at 1593 cm^{-1} and 1624 cm^{-1} correspond, respectively, to water monomers and dimers. These bands are characterized by small bandwidths, it means long dephasing times. Bigger clusters have shorter times of dissociation and, therefore, broader vibrational bands [43]. The bands at

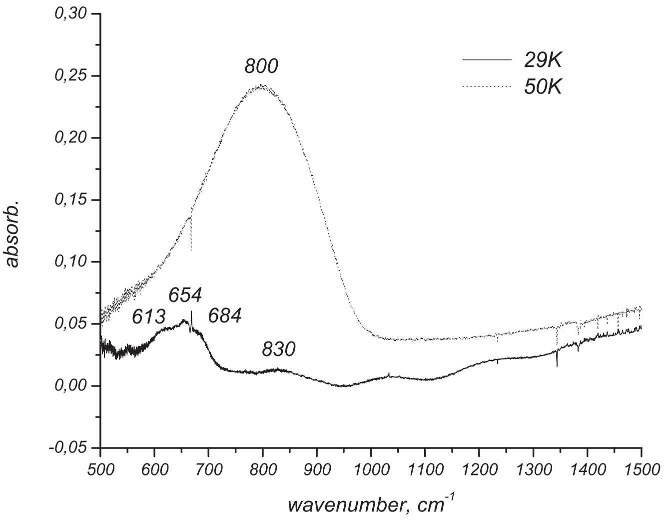

Fig. 2. FTIR spectra of water in an Ar matrix at different temperatures in the spectral region 500–1500 cm^{-1}.

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