Possible mechanism of molecular motion in liquid water from dielectric spectroscopy data

A.A. Volkov [a], V.G. Artemov [a,*], A.A. Volkov Jr [b], N.N. Sysoev [b]

[a] *A.M. Prokhorov General Physics Institute, Russian Academy of Sciences - 119991, Moscow, Russia*
[b] *Physical Department, M.V. Lomonosov Moscow State University - 119991, Moscow, Russia*

ABSTRACT

The broadband absorption spectrum of liquid water (10^3–10^{13} Hz) contains a variety of dispersion features spread far apart on the time scale – the dc conductivity, the Debye relaxation, the relaxation-2, and the *inter*molecular vibration absorption peak at 5.3 THz. In the framework of the common hydrogen-bonding paradigm, the unified description of the features is not available. In an attempt to build a unified picture, we utilize the Frenkel's idea of the oscillation-translation dynamic of particles as a fundamental type of motion inherent to liquids. We develop a model of water structure, in which the dynamics is due to diffusion of particles, neutral H_2O molecules and H_3O^+ and OH^- ions - with their periodic localizations and mutual transformations. This model establishes, for the first time, a consistent link between the quoted spectral phenomena. Such currently debatable issues, as anomalous proton mobility and autoionization of water are discussed in the light of the new model. According to the model, water possesses a huge amount of short-living counter ions. This strongly contradicts to many current views on water, but meets support in individual MD simulations.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

The intermediate position of the liquid state between gases and solids naturally implies that atoms and molecules of a liquid participate simultaneously in oscillatory and translational motions. A physical model for such motion was proposed by Frenkel' in the 1930s [1], and 30 years later it was successfully used for interpretation of the data of neutron scattering in liquid water [2]. It was assumed that each molecule participates in Brownian diffusion, being for a short time localized to oscillate in the enclosure (cage) of its neighbors.

It would seem that the combined oscillatory-translation motion, owing to its fundamental generality, ought to have become a universal touchstone for different models of water, but this did not happen. Conventional knowledge considers water as an ensemble of tetrahedral H_2O molecules, tightly held together by hydrogen bonds [3]. It is believed that the fast breaking and forming of hydrogen bonds permits water molecules to move translationally and to rotate correlatively, thus providing water its high dielectric constant and a variety of other distinct properties. A lot of models are developed able to describe the properties separately one from another; however, the problem of a concerted scenario for the different types of molecular motion is still open (see, e.g., Refs [4,5]. and references wherein). We share the point of view that "Structure and dynamics of water remain a challenge" [6]

and that "the key physics underpinning a fully predictive mode of water has yet to be identified" [7].

Our suggestion is to search the resolution of the issue in the Frenkel's gas—solid-state model of *oscillatory*-translation motion of molecules, rather than of presently commonly considered *rotational*-translation motion [8]. We proceed from that the very short life time of a hydrogen bond (of the picosecond timescale) makes it possible to consider the hydrogen bonding event as a molecular collision. In this study, we analyze the broadband absorption spectrum of liquid water in the spirit of Frenkel's gas—solid-state idea in order to find a molecular structure meeting the experimental water dielectric response.

2. Experimental data

In Fig. 1, the broadband frequency dependent dielectric response of water is presented. It is constructed according to the studies of Refs [9–12]. The top panel shows the real part of dielectric function $\varepsilon'(\nu) = \mathrm{Re}[\varepsilon(\nu)]$ and the bottom panel presents dynamic conductivity $\sigma(\nu) = \nu\varepsilon_0\varepsilon''(\nu)$, where $\varepsilon''(\nu) = \mathrm{Im}[\varepsilon(\nu)]$, ν is frequency, and ε_0 is vacuum permittivity.

Fig. 1 shows the spectra of light and heavy water in comparison. The spectra demonstrate an isotope effect, i.e., a systematic shift of the peak frequencies if H is replaced by D. There is, however, exception: the peak at 5.3 THz (marked by arrow) shows no isotope effect. Commonly, the peak is associated with translational motion of water molecules [13].
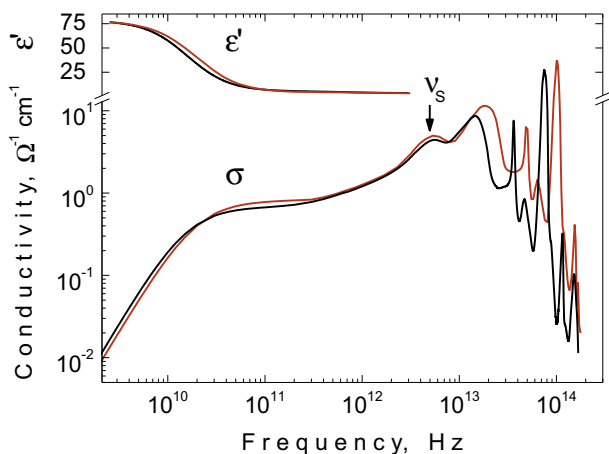
Fig. 1. Spectra of ε'(ν) and σ(ν) of liquid water at room temperature according to numerous studies [9–12]. The red and black lines correspond to H_2O and D_2O, respectively. The arrow indicates a distinctive peak at 5.3 THz (180 cm^{-1}), see text. Note the log-log scale for σ(ν).

A relevant for further discussion part of the σ(ν) spectrum which contains the 5.3 THz resonance is shown in Fig. 2. As is shown in many works (for example, in Ref. [12,14]) the dielectric response can comprehensively be described by a sum of two relaxators, R_1 and R_2, and two Lorentzians L_1 and L_2. In terms of conductivity the spectrum σ(ν) looks as:

$$\sigma(\omega) = \sigma_0 + \sum_i \frac{\sigma_i(\nu/\nu_i)^2}{1 + (\nu/\nu_i)^2} + \sum_j \frac{\sigma_j \nu^2 (\nu_j \gamma_j)^2}{(\nu_j^2 - \nu^2)^2 + (\nu \gamma_j)^2}, \quad (1)$$

where $i = 1, 2, j = 1, 2, \nu_i$ and ν_j are the characteristic frequencies, γ_j are the damping constants and σ_0 is the dc conductivity σ_{dc}. The values of the fit parameters are given in Table 1. Spectral bands R_1 and R_2 and $L_1 \equiv L_S$ are shown in Fig. 2 together with the total fit and experimental data (*intra*molecular L_2 is not relevant to our model and is not
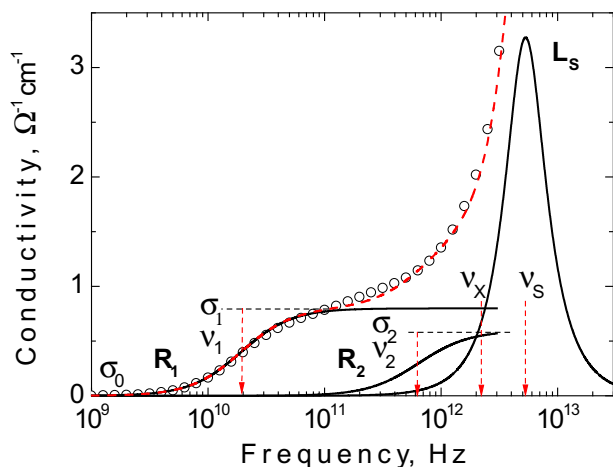

Fig. 2. Zoom-in of the conductivity spectrum from Fig. 2. Circles – experiment, red line – total fit with Eq. (1), black solid lines – contributions of terms of Eq. (1): the Debye relaxation, R_1, the relaxation-2, R_2, and the 5.3 THz peak, L_S. Fit parameters are given in Table 1. Note a scale difference as compared to Fig. 1.

Table 1
Parameters of Eq. (1) (recalculated from Ref. [12]) to fit the spectrum of Fig. 2. Additionally, $\nu_X = 2.1 \cdot 10^{12}$ Hz and $\sigma_0 \equiv \sigma_{dc} = 5.5 \cdot 10^{-6}$ Ω^{-1} m^{-1} [15].

Spectral band	R_1	R_2	L_S
Subscript, i	1	2	S
σ_i, Ω^{-1} m^{-1}	80	60	–
ν_i, 10^{12} Hz	0.02	0.64	5.3
γ_i, 10^{12} Hz	–	–	5.4

shown). As one can see, the R_1 and R_2 bands cross the L_S band (the 5 THz peak) at around $\nu_X = 2.1$ THz. In the high frequency limit R_1 and R_2 bands come to plateaus $\sigma_1 = 80$ and $\sigma_2 = 60$ Ω^{-1} m^{-1}, respectively.

The challenge is to find a molecular structure the dynamics of which will naturally provide the shape of the spectral R_1, R_2 and L_S bands.

3. Model

For the sake of clearness, the experimental spectrum of Fig. 2 is redrawn in Fig. 3 as a sketch. Similarly to Ref. [2] we consider an ensemble of H_2O molecules each of them making an oscillatory motion and also moving as free diffusing particle. In addition, we introduce into the consideration the protonated and deprotonated H_2O molecules (H_3O^+ и OH^- ions), as well as proton transfer between molecules and ions during the thermal ion-molecular collisions. An important point is that the ion motion is observable in the optical conductivity. Thus, the ions are used as indicators of the general ion-molecular motion.

A schematic diagram of the assumed structure is shown in Fig. 4. The elementary dynamic processes are labeled with numbers in Figs. 3 and 4. For example, the process number 1 indicates the oscillation motion of an H_3O^+ ion with a thermal frequency of ν_S inside a hydration cage [16]. We will refer to such ions surrounded with a hydration cage as "dressed". Their concentration will be N_S. The concentration of neutral H_2O molecules and the total ion concentration are N_W и N_I, respectively.

With a frequency ν_X the charge (excess proton) jumps to the edge of the cage where has a probability to go beyond the cage, to become undressed (process 2). The leaving charge transfers over a number of H_2O molecules and in the time t_U gets localized, becoming dressed again (process 4). For the time t_U the hydration cage (as a polarization configuration of water molecules) transfers to the distance l. Let the concentration of the bare charges be N_U, so that $N_I \equiv N_C = N_S + N_U$, where N_C is the concentration of the cages.

The H_2O molecule left by the charge (shown gray in Fig. 3) diffuses as a neutral particle during the time t_W (process 5) until it meets an ion, picks up the ion's charge (excess proton) and forms a hydration cage about itself (transforms into a hydrated ion). Hydration on the very long scale of t_W happens instantly, so that the molecular configuration comes back to the initial oscillation state 1 (process 5').

In accordance with the above, let us correlate the times t_W, t_U and others related to Fig. 4 for the dispersion features of the conductivity spectrum σ(ν) in Figs. 2 and 3. The following times can be defined as the lifetimes of.

$t_S = \nu_S/\nu_X^2$ – a charge in the intact hydration cage;
$t_U = 1/\nu_2 - 1/\nu_X$ – a charge in the destroying hydration cage;
$t_W = 1/\nu_1 - 1/\nu_X$ – a neutral H_2O molecule;
and $t_I = t_S + t_U$ – a diffusion time of the hydrated charge.
The balance equations can be written, in view of $N_0 >> N_I$, as:

$$N_W/t_W = N_I/t_I \quad \text{and} \quad N_U/t_U = N_S/t_S \quad (2)$$

where $N_W = N_0 - N_I$ and $N_0 = 55.5$ mol/l $= 3.3 \cdot 10^{28}$ m^{-3} is a total concentration of particles in liquid water. The quoted life times and concentrations calculated from Eq. (2) are presented in Table 2.

The abnormally high ion concentration stands out, $N_I = 1.5 \cdot 10^{27}$ m^{-3} (4.5% of total number of particle). This value is consistent with that obtained by us in Ref. [17]: there are 22 H_2O molecules per one ion. The