ELSEVIER

Influence of temperature on wideband water spectra: Semi-phenomenological calculation

Vladimir I. Gaiduk [a,*], Derrick S.F. Crothers [b]

[a] *Institute of Radio Engineering and Electronics, Russian Academy of Sciences, Vvedensky Sq. 1, Fryazino 141190, Moscow region, Russia*
[b] *Queen's University Belfast, Belfast BT7 1NN, Northern Ireland, UK*

Abstract

The results of analytical calculation of the complex permittivity ε and of the absorption coefficient α are presented for the temperature range extending from $-5.6\ °C$ for supercooled water to $81.4\ °C$. Dielectric response is modeled by two water fractions with lifetimes from 0.1 to 0.25 ps. One fraction comprises rigid permanent dipoles librating rather freely in a narrow and deep hat-like potential well and the other fraction comprises H-bonded charged molecules performing: (a) fast elastic vibrations along the hydrogen bond; (b) elastic reorientations around this bond; and (c) non-harmonic bending vibration perpendicular to the H-bond. At low temperature the latter vibration is characterized by a noticeable association of water molecules. The calculation reveals the break in continuity of some fitted model parameters occurring in water at the temperature $\approx 300\ K$.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Water; Supercooled water; Complex permittivity; Absorption coefficient; Dielectric relaxation; Association; Analytical theory; Libration; Vibration; Permanent dipole; Nonrigid dipole; Hydrogen bond

1. Introduction

Studies of dielectric spectra of water present a fundamental physical problem that has also important practical applications. Experimental investigation of these spectra has a rich history. We refer here only to a few works [1–5]. In [1,2], tables for optical constants of water were presented for the temperature $T = 300\ K$ and in a wide T-range, respectively. In recent publications [3,4] in addition to original investigations, the results of many other works are also discussed. In [5] a useful empirical double Debye–double Lorentz formula for the complex permittivity $\varepsilon(v, T)$ was suggested.

The key theoretical problem consists in the difficulty of an adequate interpretation of the influence of temperature on the permittivity $\varepsilon(v)$ and absorption coefficient $\alpha(v)$.

Recently agreement of experimental and theoretical spectra of water was achieved, using:

(a) a molecular dynamics (MD) simulation, based on consideration of pair interactions in a large assembly of water molecules (see e.g. [4] and references therein)
(b) a semi-phenomenological (SP) approach [6,7].

The first (MD) approach actually comprises a computational experiment. Being, perhaps, the most fundamental, the MD simulation has however some restrictions, such as complexity, high cost of computation and inapplicability for calculation of the low-frequency spectra. Moreover, the MD simulation gives only a quantitative agreement with experiment. These drawbacks are avoided in the analytical SP approach, which is however less fundamental than the MD simulation. Indeed, the effective potentials, in which rigid or nonrigid dipoles move, are introduced in SP models on an *intuitive* basis. In this work the SP approach will be used for calculation of water spectra.

* Corresponding author. Tel.: +7 496 56 429 36; fax: +7 495 702 9572.
  E-mail addresses: vigaiduk@mail.ru (V.I. Gaiduk), d.crothers@qub.ac.uk (D.S.F. Crothers).
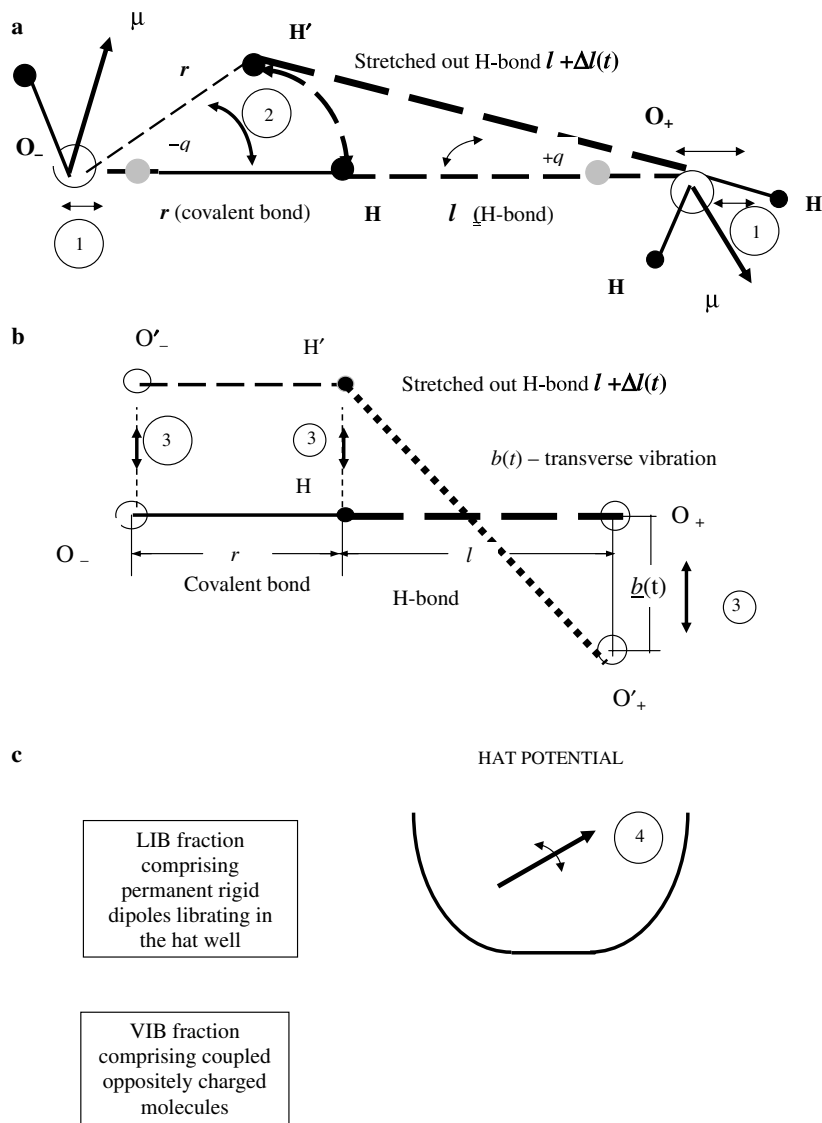
Fig. 1. (a and b) The schemes of the dimer performing (a) harmonic translations/reorientations and (b) non-harmonic transverse vibrations. (c) The scheme pertaining to the mixed model of water/ice. 1, Harmonic longitudinal vibration of the oxygen atoms generates the translational band. 2, Harmonic reorientation of the permanent dipole generates the V-band located nearby the translational band. 3, Non-harmonic transverse vibration of the oxygen atoms generates the low-frequency wing of the V-band in the THz region. 4, Nonharmonic libration of permanent dipole in the hat potential determines the far-infrared librational and the microwave relaxational bands; with the decrease of temperature the potential profile becomes close to the parabolic one.

1.1. Features of the semi-phenomenological approach

Unlike previous works, e.g. [6,7], to calculate the complex permittivity we employ a new approach, first published in [8,9], substantially modified in [10], and recently supplemented [11] with the additional mechanism of transverse vibrations (TV). Here the calculation scheme employed in [11] for two temperatures will be used for water in the range from −5.6 to 81.4 °C, notations T and T_C are used for temperature expressed in K and °C, respectively.

We consider a two fractional (mixed) model of water spectra[1] comprising the librational (LIB) and vibrational (VIB) states illustrated by Fig. 1c.

1.1.1. The LIB state

This state describes, just as was made previously [6,8–11]

- dielectric response arising from libration of a permanent dipole μ in a hat-like potential well; the relevant librational band is located near the border of the infrared region (at $\approx 700 \text{ cm}^{-1}$) and
- the non-resonant relaxation band, whose loss peak is located at microwaves.

The lifetime τ_{or} of the LIB state is much less than a picosecond.

In accord with [8] during *cooperative* fast reorientations of hydrogen atoms, occurring inside a rather stable tetrahedral-like set of oxygen atoms, some "favorable"

---

[1] Our theory could also be applied to ice I_h [10].