

# Analytical calculation of far infrared spectra of ice in terms of a molecular model

V.I. Gaiduk<sup>a,\*</sup>, B.M. Tseitlin<sup>a</sup>, D.S.F. Crothers<sup>b</sup>

<sup>a</sup>*Institute of Radio Engineering and Electronics, Russian Academy of Sciences, Vvedensky Sq. 1, Fryazino, 141190 Moscow region, Russia*

<sup>b</sup>*Queen's University Belfast, Belfast BT7 1NN, Northern Ireland, UK*

Received 9 October 2004; revised 28 October 2004; accepted 28 October 2004

## Abstract

Wideband far infrared (FIR) spectra of complex permittivity  $\varepsilon(\nu)$  of ice are calculated in terms of a simple analytical theory based on the method of dipolar autocorrelation functions. The molecular model represents a revision of the model recently presented for liquid water in *Adv. Chem. Phys.* 127 (2003) 65. A composite two-fractional model is proposed. The model is characterised by three phenomenological potential wells corresponding to the three FIR bands observed in ice. The first fraction comprises dipoles reorienting in a rather narrow and deep hat-like well; these dipoles generate the librational band centred at the frequency  $\approx 880 \text{ cm}^{-1}$ . The second fraction comprises elastically interacting particles; they generate two nearby bands placed around frequency  $200 \text{ cm}^{-1}$ . For description of one of these bands the harmonic oscillator (HO) model is used, in which translational oscillations of two charged molecules along the H-bond are considered. The other band is produced by the H-bond stretch, which governs hindered rotation of a rigid dipole. Such a motion and its dielectric response are described in terms of a new cut parabolic (CP) model applicable for any vibration amplitude.

The composite hat-HO-CP model results in a smooth  $\varepsilon(\nu)$  ice spectrum, which does not resemble the noise-like spectra of ice met in the known literature. The proposed theory satisfactorily agrees with the experimental ice spectrum measured at  $-7^\circ\text{C}$ . The calculated longitudinal optic-transverse optic (LO-TO) splitting occurring at  $\approx 250 \text{ cm}^{-1}$  qualitatively agrees with the measured data.

© 2004 Elsevier B.V. All rights reserved.

**Keywords:** Dielectric response; Complex dielectric permittivity; Absorption coefficient; H-bond; Liquid water; Ice Ih; Autocorrelation function; Libration; Hindered rotation; Parabolic potential; Proton jump

## 1. Introduction

### 1.1. The problem

A fundamental problem concerning the theory of far infrared (FIR), Raman and other spectra of ice, especially of ice Ih, whose structure is similar to that of liquid water, is discussed in many works, e.g. in [1–3], see also references therein. Existing theories, based on the lattice mode spectroscopy, being extremely complex and non-transparent, yield a qualitative description of the complex permittivity  $\varepsilon$  in the bands near  $200 \text{ cm}^{-1}$ . A poor

description of spectra is obtained for the librational band placed near  $900 \text{ cm}^{-1}$ . In the theory [1–3] all bands comprise a multitude of narrow noise-like patterns, while the experimental spectra are rather smooth [1–4].

In view of evident similarity of the FIR spectra in ice [1–4] and in water [5,6], which could be explained by similarity of their structures, the following questions arise: is it possible to (i) obtain *smooth* spectra of the complex permittivity *also* for ice and (ii) describe analytically the wideband FIR spectra in terms of a molecular model [7] employed for water. The aim of this work is to prove this possibility using the method of dipolar autocorrelation functions (ACF) [8].

Two-fractional models [7] provide an agreement between the theoretical and experimental spectra of water  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  in the range  $0\text{--}1000 \text{ cm}^{-1}$ . However, in the case of ice three peaks (not two, as in the case of water) of the loss factor  $\varepsilon''(\nu)$  are observed in the FIR range: a double

*Abbreviations:* ACF, autocorrelation function; CP, cut parabolic; FIR, far infrared; SF, spectral function.

\* Corresponding author. Tel.: +7 96 564 2936; fax: +7 95 702 9572.

E-mail address: [vigaiduk@nail.ru](mailto:vigaiduk@nail.ru) (V.I. Gaiduk).

peak at  $\nu \approx 200 \text{ cm}^{-1}$  and a peak at  $\approx 900 \text{ cm}^{-1}$  (the wavenumber  $\nu$  is termed ‘frequency’). These experimental facts propel us to modify modelling of the FIR spectra of ice, as well as of water. A difference of models proposed for both fluids concerns only the low-frequency spectrum (the latter unlike that of water is not examined for ice).

### 1.2. An approach for modelling of wideband spectra

A one-particle approximation is used. A motion of a polar molecule in a *given* static potential is basically regarded as a rigid-dipole rotation or translational oscillations of charged particles. The employed potentials are actually *quasi-static*, since they are characterised by the mean lifetime  $\tau$ , whose inverse quantity  $\tau^{-1}$  is proportional to a molecular-friction coefficient. The lifetimes  $\tau$  of the employed potentials are less than 1 ps and thus are much shorter than the Debye relaxation time  $\tau_D$ . Dielectric response of a chosen molecular motion is found using the ACF method, whose central point consists in calculation of the *spectral function* (SF)  $L(z)$ . The latter is linearly related to the *spectrum* of a dipolar ACF,  $z$  being the reduced complex frequency; see, e.g. Eq. (2.4). The potential profiles are chosen using physical reasoning<sup>1</sup> aided by comparison of theoretical and experimental spectra. For any particular potential a linear-response theory is given without reference to other potentials.

### 1.3. The model for the librational band

Retaining the same approach for water and ice, we assume: (i) most of the dipoles librate rather freely in a hat-like intermolecular potential; (ii) some of the H-bonds are strongly bent or torn. Molecular rotation in such a well is termed *reorientation*. The hat potential has a flat bottom followed by steeply rising parabolic walls; the corresponding spectral function  $L_{\text{or}}(z)$  was first given (without derivation) in Ref. [10]; a more sophisticated theory was presented in Refs. [7,11]. In this work a substantially simplified formula for this SF is used, Eqs. (2.16)–(2.18).

### 1.4. Ensembles of molecules, which undergo elastic interactions

The dipoles rotating in the hat well comprise one of two fractions. The rest particles, which amount to 8–14%, belong to the second fraction. We term *vibration* relevant molecular motions in order to distinguish them from reorientations of dipoles in the hat well. We consider for vibration two dielectric-response mechanisms (their interrelation is ignored). Correspondingly, we find two spectral

functions,  $L_q(Z_q)$  and  $L_\mu(Z_\mu)$ . The first,  $L_q$ , concerns translational oscillations<sup>2</sup> of a *non-rigid dipole*, which appears due to proton jumps (see Section 4). The second SF,  $L_\mu$ , ascribed to hindered rotation of a rigid polar molecule, is calculated for a new phenomenological cut parabolic (CP) model applicable for any vibration amplitude. The CP well does not involve (unlike the hat well) a flat part on the potential bottom.

In this work the FIR spectra of water at 27 °C and of ice at –7 °C are calculated and compared; we examine the change of the FIR spectrum due to transition from *liquid* to *solid* state. For water we consider the entire range 0–1000  $\text{cm}^{-1}$  of orientational/translational relaxation. For ice we concentrate our attention on the FIR range 50–1000  $\text{cm}^{-1}$ .

## 2. The calculation scheme

### 2.1. Formulae for the complex permittivity and susceptibility [7]

We employ the following molecular parameters: moment of inertia  $I$ ; molecular mass  $M$ ; optical permittivity  $n_\infty^2$  referring to the high frequency edge of the FIR region; dipole moment of a molecule in vacuum  $\mu_0$ ; static permittivity  $\epsilon_s$ ; Debye relaxation time  $\tau_D$ ; density  $\rho$ ; dipole-moment factor  $k_\mu$  (close to 1), which connects  $\mu_0$  with dipole moment  $\mu$  of a molecule in polar fluid as

$$\mu = (1/3)\mu_0 k_\mu (n_\infty^2 + 2). \quad (2.1)$$

We represent the complex permittivity  $\epsilon^*(\nu) = \epsilon'(\nu) + i\epsilon''(\nu)$  and the total concentration  $N$  as sums of terms pertinent to reorienting and vibrating dipoles. The permittivity  $\Delta\epsilon^*(\nu)$ , pertinent to the latter, comprises the part  $\Delta\epsilon_\mu^*(\nu)$ , related to hindered rotation of rigid dipoles, and the part  $\Delta\epsilon_q^*(\nu)$ , produced by elastic vibration of charged particles, comprising non-rigid dipoles:

$$\epsilon^*(\nu) = \epsilon_{\text{or}}^*(\nu) + \Delta\epsilon^*(\nu); \quad \Delta\epsilon^*(\nu) = \Delta\epsilon_\mu^*(\nu) + \Delta\epsilon_q^*(\nu), \quad (2.2)$$

$$N = N_{\text{or}} + N_{\text{vib}}. \quad (2.3)$$

Taking into account that  $\epsilon = \epsilon' - i\epsilon''$ , we employ the complex-conjugation symbol in order that  $\text{Im}(\epsilon^*)$  give us the dielectric loss-factor  $\epsilon''$ . To simplify designations we omit the symbol  $*$ ; so below we mean  $\epsilon = \epsilon' + i\epsilon''$ . Analogously we change notation for the complex susceptibility  $\chi^*$ .

We introduce the proportion  $r_{\text{vib}} \equiv N_{\text{vib}}/N$  of *vibrating* molecules (*rigid* dipoles), affected by the cut parabolic potential and characterised by the lifetime  $\tau_{\text{vib}}$  and the SF  $L_\mu(Z_\mu)$ . Thus the concentration of *reorienting* rigid dipoles

<sup>1</sup> An important exception comprises the work [9], in which one of two potentials is calculated from consideration of elastic interactions occurring in the dimer of rotating water molecules.

<sup>2</sup> Analogous studies were made in Refs. [7,10,12] for description of the 200  $\text{cm}^{-1}$  band in water.

Download English Version:

<https://daneshyari.com/en/article/9770318>

Download Persian Version:

<https://daneshyari.com/article/9770318>

[Daneshyari.com](https://daneshyari.com)