On optimization of absorption−dispersion spectra

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ABSTRACT

A modified approach to the analysis of spectra of the complex electric permittivity of liquids in the Infrared region is presented. These spectra are derived from experimental spectra of the complex refractive index. Subsequently they are used to determine important secondary quantities, e.g. spectra of complex molecular polarizabilities and an integral property − the molar vibrational polarization. The accuracy of these quantities depends essentially on the accuracy of both components of the complex electric permittivity spectrum.

In the proposed procedure, the spectra of the complex electric permittivity are approximated using the Classical Damped Harmonic Oscillator (CDHO) model for the description of individual bandshapes. The CDHO model defines both the real and imaginary part of the complex permittivity. The fitting procedure includes a simultaneous optimization of both the real and imaginary parts of the complex permittivity spectrum. A comparison of absorption-only curve fitting and the novel absorption-dispersion double curve fitting is presented; advantages of the new approach in accuracy, reliability and convergence time are pointed out.

Due to the complexity of the problem, the choice was restricted to non-gradient methods of optimization. The performance of several gradientless algorithms was tested. Among numerous procedures the Powell General Least Squares Method Without Derivatives was found to be the most efficient. The reliability of obtained results of the band separatiovn process was tested on several simulated spectra of increasing complexity.

The applicability of the developed approach to the analysis of exemplary experimental data was evaluated and discussed.

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1. Introduction

An important goal of infrared dispersion studies of liquids is to determine high−frequency dielectric properties originating from internal vibrations of the molecule. The determination of these properties requires the precise knowledge of the spectra of both components of the complex refractive index in the relevant spectral region (ν denotes wavenumbers [cm^{-1}] throughout this work and $i = \sqrt{-1}$):

$$\widehat{n}(\nu) = n(\nu) + ik(\nu) \tag{1}$$

Here the real part $n(\nu)$ denotes the spectrum of the refractive index and the imaginary part − $k(\nu)$ − the spectrum of the absorption index; both spectra are dimensionless. Various methods

for experimental determination of optical constants were described by Bertie [1]. In general, it is not easy to obtain accurate experimental data. In our studies we determine these spectra following an approach based on transmission spectroscopy in broad frequency range, covering the Visible (VIS), Near Infrared (NIR), Mid Infrared (MIR) and Far Infrared (FIR) regions [2]. The main difficulty with this method stems from the fact, that very thin films have to be used in the MIR region to obtain reliable quantitative data.

From the spectra of both components of the complex refractive index the spectrum of the complex electric permittivity is obtained:

$$\widehat{\varepsilon}(\nu) = \varepsilon\prime(\nu) + i\varepsilon''(\nu) \tag{2}$$

in the studied spectral regions following Maxwell's relations. These spectra describe the high-frequency dielectric properties of the studied liquid. Basing on them, important secondary quantities can be determined.

From the spectrum of the complex electric permittivity (Eq. (2)) the spectrum of the complex molecular polarizability, $\widehat{\alpha}(\nu)$, can be

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obtained:

$$\widehat{\alpha}(\nu) = \alpha'(\nu) + i\alpha''(\nu) \tag{3}$$

where $\alpha'(\nu)$ is the spectrum of the dispersive part and $\alpha''(\nu)$ - the spectrum of the absorptive part of the complex polarizability function. The separation of the real and imaginary parts are performed assuming a model for the local electric field in the dielectric, e.g., the Lorentz field leading to the Clausius-Mossotti equation [1,3] in the form:

$$\frac{\widehat{\varepsilon}(\nu) - 1}{\widehat{\varepsilon}(\nu) + 2} \cdot \frac{M}{d} = \frac{4}{3}\pi N_A \widehat{\alpha}(\nu) \tag{4}$$

By separation of the real and imaginary parts of the complex molecular polarizability (Eq. (3)) assuming this field, expressions for $\alpha'(\nu)$ and $\alpha''(\nu)$ can be obtained:

$$\alpha'(\nu) = \frac{3V_m}{4\pi} \frac{(\varepsilon'(\nu) - 1)(\varepsilon'(\nu) + 2) + \varepsilon''(\nu)^2}{(\varepsilon'(\nu) + 2)^2 + \varepsilon''(\nu)^2} \tag{5}$$

$$\alpha''(\nu) = \frac{9V_m}{4\pi} \frac{\varepsilon''(\nu)}{(\varepsilon'(\nu) + 2)^2 + \varepsilon''(\nu)^2} \tag{6}$$

where V_m denotes the molar volume of the liquid, Md^{-1}, where M is the molar weight in [g mol^{-1}] and d the density of the liquid in [g cm^{-3}].

An important quantity in dielectric studies is the molar vibrational polarization P^{vib} related to a particular spectral range, or − even more desirably − to a particular mode.

$$P^{vib} = \left(\frac{\varepsilon'_l - 1}{\varepsilon'_l + 2} - \frac{\varepsilon'_h - 1}{\varepsilon'_h + 2} \right) V_m \tag{7}$$

In this relation, ε'_l and ε'_h are values of the real component of the electric permittivity at respectively the low-frequency and high-frequency side of the relevant band (or spectral range). It is advantageous to determine the values of ε'_l and ε'_h possibly in "flat" regions of the $\varepsilon'(\nu)$ spectrum, i.e. at points in regions of normal dispersion; however it is usually not possible to find satisfactory spots. In practice, it is more convenient to calculate the dielectric increment $\Delta\varepsilon\prime = \varepsilon'_l - \varepsilon'_h$ [4]:

$$\Delta\varepsilon' = \frac{2}{\pi} \int_{\nu_l}^{\nu_h} \frac{\varepsilon''(\nu)}{\nu} d\nu \tag{8}$$

In this expression, ν_l and ν_h describe the limits of integration over the absorption band (or group of bands). Since $\varepsilon'_l \cong \varepsilon'_h$, the expression for vibrational polarization (Eq. (7)) can be reduced to:

$$P^{vib} = \frac{\Delta\varepsilon'}{\varepsilon'_h + 2} \frac{M}{d} \tag{9}$$

2. The bandshape function

In the majority of spectroscopic applications, data for individual absorption bands are desired. Since the bands are usually overlapping, appropriate separation procedures have to be applied. In such procedures, suitable band models have to be used. Usually only the absorptive parts of the complex spectra were optimized. Numerous band models, basing mainly on the Cauchy (Lorentz) and Gauss functions and their combinations were proposed and advanced optimization techniques performing the fitting process

were developed in the past [5,6] and are currently used in commercial software.

However, for several purposes both components of the complex electric permittivity function (Eq. (2)) are needed for each band. This stimulated us to develop an algorithm for simultaneous optimization of the: $\varepsilon'(\nu)$ and $\varepsilon''(\nu)$ curves. Each band was described by the well known Classical Damped Harmonic Oscillator (CDHO) [7] model specified in Eq. (10). In our approach parameters for each band and also ε_∞, the parameter valid for the entire studied spectrum, were optimized.

$$\widehat{\varepsilon}(\nu) = \varepsilon_\infty + \sum_{j=1}^{N} \frac{S_j^2}{\nu_j^2 - \nu^2 + i\nu\gamma_j} \tag{10}$$

After separation of the real and imaginary parts we obtain:

$$\varepsilon'(\nu) = \varepsilon'_\infty + \sum_{j}^{N} \frac{S_j^2 \left(\nu_j^2 - \nu^2 \right)}{\left(\nu_j^2 - \nu^2 \right)^2 + \gamma_j^2 \nu^2} \tag{11}$$

$$\varepsilon''(\nu) = \sum_{j}^{N} \frac{S_j^2 \gamma_j \nu}{\left(\nu_j^2 - \nu^2 \right)^2 + \gamma_j^2 \nu^2} \tag{12}$$

In the above equations, S_j denotes the „oscillator strength" related to the peak height of the j-th band, ν_j its resonant wavenumber and γ_j the damping constant related to the half-width of the band. In the above notation S_j, ν_j, γ_j have the same dimension (cm^{-1}). N denotes the number of bands.

From equations (Eq. (11)) and (Eq. (12)) model $n(\nu)$ and $k(\nu)$ spectra can be easily calculated following Maxwell's equations. Let's note that the $\varepsilon''(\nu)$ and $k(\nu)$ absorption curves resulting from the above model are not symmetrical; what's more, the band maxima of both curves do not coincide.

The CDHO model is a physical model, derived on the basis of the local Lorentz field. The basic features of the model are the facts, that both components of the spectrum − i.e. its real and imaginary parts − are analytically defined and fulfil the Kramers−Krönig relations [8]. As the consequence, the CDHO model has an essential advantage over the purely numerical bandshape models widely used in modelling of spectra and in band separation software.

3. Computational procedures

The aim of this work was to obtain a possibly most accurate description of the spectra of the complex electric permittivity of a liquid in the Mid-Infrared range. The procedure enables a new insight into the molar vibrational polarization analysis. Up to now, the molar vibrational polarization P^{vib} could be only determined for separated, limited spectral ranges, for which its boundaries lie in the normal dispersion region. As such, the determination of contributions of individual bands into total P^{vib} was possible only for very rare cases of isolated bands. The method should allow to obtain spectral data for each band in the complex permittivity spectrum and to determine the contribution to P^{vib} for each band to the total molar vibrational polarization.

The method described in detail in this work is based on a simultaneous optimization of spectra of both components of the complex electric permittivity, with the benefits of increased efficiency of the process and reliability of the results. Hitherto, in papers reported in literature, only the absorption spectra, i.e. $k(\nu)$, $\varepsilon'(\nu)$ or $\alpha''(\nu)$ were optimized, to our best knowledge. For a spectrum consisting of considerably overlapping bands it may result in less-accurate or even unreliable solutions, resulting from the fact, that