On optimization of absorption—dispersion spectra.

Autorzy

Jerzy P. Hawranek

Justyna E. Grabska

Krzysztof B. Beć

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Streszczenie

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.

Słowa kluczowe

IR dispersion of liquids, IR dielectric function, Classical damped harmonic oscillator model, Band fitting