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Band shape determination with robust estimator based on continuous wavelet transform

S.S. Kharintsev *, D.Z. Galimullin, A.Yu. Vorob'ev, M.Kh. Salakhov

Department of Physics, Kazan State University, Kremlevskaya Str., 16, Kazan 420008, Russia

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Abstract

The paper focuses on an alternative approach that allows one to identify overlapping band shapes with the help of the continuous wavelet transform (CWT). We show that less number of special points for determining a band shape is required unlike the fractional derivative spectrometry method [S.S. Kharintsev, M.Kh. Salakhov, Spectrochim. Acta Part A, 60 (2004) 2125]. Besides, the CWT-based derivative spectrometry can be successfully utilized in a case of complex spectra corrupted with a white and/or high-frequency noise. The power of this method is illustrated on model examples and experimental spectra of 1,2-diphenylethane in crystalline and melted phase.
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Keywords: Band shape; Decomposition; Continuous wavelet transform; Fitting

1. Introduction

The knowledge of a number of overlapping bands in complex spectra and their shapes is of the greatest importance for correctly assigning bands in terms of the conventional least squares method (LSM). As it is known, the derivative spectrometry (DS) method, based on numerical differentiation [2–9], is widely used in practice as a reliable instrument for finding a number of latent components. However, a question on bands' shape determination is still open because this problem is ambiguous and, therefore, ill-posed [2,5].

Nowadays, there are a lot of different numerical algorithms for solving this problem (see, for example, [2]). In general, they belong to either a parametric approach, including determination of parameters for a given mathematical model, or an approach, implying a certain transformation of an analytical signal. The first one is to minimize a functional $M[F]$ of the form:

$$M[F] = \sum w_i [I(x_i) - F(x_i, \vec{a})]^2, \quad (1)$$

where w_i are the weights ($i = 1, \ldots, N$, N is a number of points), $I(x_i)$ a radiation or absorption band in the spectrum observed at wavenumber x_i, $F(x_i, \vec{a})$ is a fitting function with a set of parameters $\vec{a} = \{a_1, \ldots, a_M\}$. Different modifications of LSM can be used for minimizing functional (1). One should note that experimental errors are inevitably present in spectra observed and LSM is extremely sensitive to both an initial approximation and noise. To overcome these drawbacks, a sought solution should be regularized on the basis of all available a priori information [10].

The second approach is reduced to the transformation of a band I under analysis to a new representation J in terms of basis functions $\varphi(x)$:

$$I(x) = \sum_k J_k \varphi_k(x). \quad (2)$$

The basis functions may be derivatives (including fractional ones), orthogonal functions, moments, wavelets, elementary curves (Guassian, Lorentzian, etc.). As a result of transformation (2), spectrum $I(x)$ is replaced by a "spectrum" of derivatives, polynomials, wavelets, Fourier transforms, etc. described by the vector J_k. These transformations underlie the DS method, the Fourier- and wavelet-based method, the algebraic correction of background, the moments method and neural networks and others [2,5].

Among them, the DS method is most commonly used in analytical spectroscopy for linear transformation of spectra, improving resolution, and thereby, permitting determination of spectral parameters. A popularity of DS is due to both its analytical properties and similarity of original spectra and their even derivatives shapes. In particular, because of the considerable increase in the

* Corresponding author. Tel.: +7 8432 315173; fax: +7 8432 387044.
E-mail addresses: red@ksu.ru (S.S. Kharintsev), msalakh@ksu.ru (M.Kh. Salakhov).

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