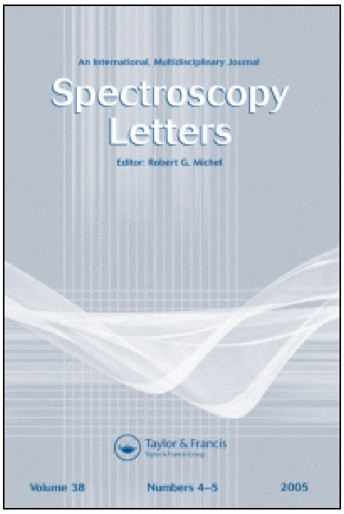

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Differentiation of Electronic Absorption Spectra Complicated by Vibronic Fine Structure

Józef Myrczek[a]
[a] Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Technical University of Wrocław, Wrocław, Poland

To cite this Article Myrczek, Józef(1989) 'Differentiation of Electronic Absorption Spectra Complicated by Vibronic Fine Structure', Spectroscopy Letters, 22: 1, 79 — 86

To link to this Article: DOI: 10.1080/00387018908053861

URL: http://dx.doi.org/10.1080/00387018908053861

SPECTROSCOPY LETTERS, 22(1), 79-86 (1989)

DIFFERENTIATION OF ELECTRONIC ABSORPTION SPECTRA COMPLICATED BY VIBRONIC FINE STRUCTURE

key words: differentiation, spectral contours, vibronic spectra

Józef Myrczek

Institute of Inorganic Chemistry and Metallurgy of Rare
Elements, Technical University of Wrocław, Wybrzeże
Wyspiańskiego 27, 50-370 Wrocław, Poland.

ABSTRACT

An influence of the distance of measured points on results of Savitzky-Golay method of spectral contour differentiation was investigated. Some conclusions based on the differentiation of electronic absorption spectra with vibronic structure were formulated.

INTRODUCTION

Numerical differentiation of spectra is very common and new methods are still developed (e.g.[1-6]). The main advantage of differentiation is detection of very weak and/or strongly overlapping bands. The main extrema of the even order derivative (as well as zero values of the odd derivatives) correspond to the positions of component bands. A shape of an analytical curve of the second derivative of a symmetrical band (like Gaussian or Lorentzian) is very characteristic (e.g.[6]). The maximum of an original bandshape is represented by the narrower minimum of the second derivative, so the structure of the original spectral contour could be enhanced. However, numerical calculation of the derivative could give only an approximate shape but not the exact analytical curve.

In this communication we present the results of our study of an influence of the interval between measured points on the results of the differentiation by Savitzky-Golay method.[7] The investigated spectra were electronic absorption spectra with vibronic structure consisted of strongly overlapped narrow and broad bands. Therefore, a resolution of such spectra is difficult and demands a very careful treatment.

EXPERIMENTAL

The following electronic absorption spectra were taken into consideration:

- $KMnO_4$ in water solution[8] ,
- $KCrO_3Cl$ in acetone and acetonitrile solutions[9] ,
- chromyl chloride and chromyl borate in acetone and acetone+CCl_4 [10],
- several Cr^{IV}complexes in formamide, dimethylformamide and acetonitrile [10,11]

and a number of simulated (theoretical) spectra.

The spectra were recorded at room temperature with Hitachi 356 UV/VIS spectrophotometer connected to an IBM PC/XT. The spectra were smoothed with the purpose of noise reduction and differentiated using Savitzky-Golay function[7](Eq.1.).

$$Y'(i)=(1/252\Delta)*[22(Y(i-3)-Y(i+3))-67(Y(i-2)-Y(i+2))-58(Y(i-1)-Y(i+1))] \quad (1)$$

where Y(I) is the spectral value at the equidistanced measured points and Δ is this distance (so-called derivatization interval).

The second derivative of spectra was obtained by using two passes of a first derivative procedures, according to Gans and Gill[5] (two passes of a first derivative filter gave slightly better results than one pass of a second derivative function for Lorentzian and Gaussian bandshapes).

All the computer programs were written in FORTRAN.

RESULTS AND DISCUSSION

A typical example of the second derivative of the investigated spectra is displayed on Fig.1. The spectral contour consists of 29 bands. A method of resolution into component bands was described in[8,9]. Parameters of these bands were listed in paper[8]. Some of the bands are broad and structureless, other exhibit vibrational fine structure. The contours of narrow vibronic component bands (with semi halfwidths below 500cm^{-1}) are represented by their maximum intensities only in Fig.1a.

If Δ value is very small (and a noise is not reduced) then the differentiation of the spectrum gives a lot of local extrema which do not correspond to the features of spectrum and makes a "noisy" resultant curve only. Therefore it was very difficult to draw it.

A result of differentiation with Δ=50cm^{-1} i displayed on Fig.1b. The minima correspond to th narrow component bands of vibronic structure. The broa

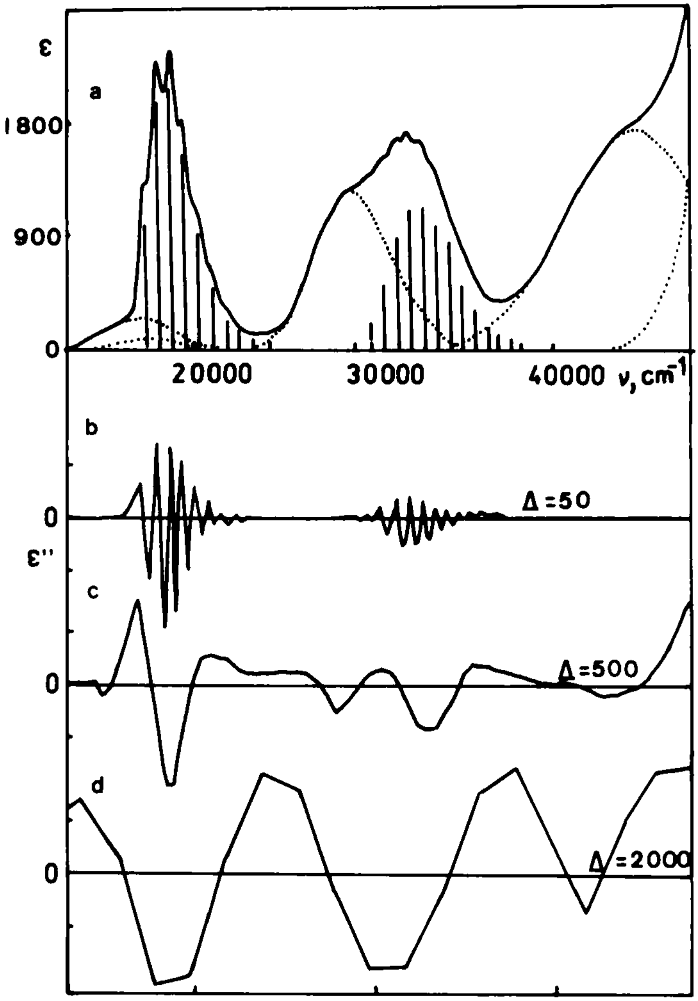

FIG.1. a) Component bands of the vibronic spectrum of kalium permanganate in water[8],
b-d) The second derivative of the spectrum calculated for different values of Δ parameter.

bands are not detected in this way. In effect the fine structure could be investigated and some important physicochemical parameters calculated e.g. positions of progression members according to harmonic or anharmonic oscillator approximations. However, the presence of electronic bands are neglected in this case.

Differentiation with $\Delta=500cm^{-1}$ is shown on Fig.1c. The previously detected narrow bands of vibronic structure are now neglected. The minima correspond to the broad electronic bands and not to their vibronic structure even it occurs in original spectrum. Therefore, the fine structure can not be studied but the positions of electronic bands are well established.

The results of differentiation with $\Delta=2000cm^{-1}$ are shown on Fig.1d. The next spectrum features have been lost. Only three minima are observed which correspond to groups of strongly overlapped bands (e.g. in the range of $25000-35000cm^{-1}$ only one minimum is seen in spite of two broad electronic bands; one of these bands consists of a number of narrow vibronic members).

As one can notice from the above example, the interval of measured points Δ is a critical parameter for the differentiation of spectra using Savitzky-Golay method. The same results were obtained for the other experimental and simulated spectra under consideration.

The following approximate rule was established from our investigations: For the detection of any component band in spectral contour one should take the value of Δ parameter not higher than semi halfwidth of the band and not smaller than about 1/10 of it for the second derivative. If one takes the value of Δ parameter too small or too high no proper minima at the position of the component bands could be obtained and even the occurence of the well resolved bands could be neglected. To obtain as much as possible information one should choose the values of Δ parameter very carefully and perform the process several times. In this way a detection of component bands of different halfwidths and then the physicochemical interpretation or determining the initial value of band parameters for spectral contour resolution procedures are possible.

The similar conclusion can be formulated for other differentiation methods, other even and odd orders of derivative and different spectral ranges. Maddams and Mead[1] investigated a very limited theoretical case of simulated doublets of two Lorentzian profiles of unit intensity, unit semi halfwidth and with their maxima separated by one semi halfwidth. The authors found that optimum values of derivatization interval was in the range 0.20-0.30 for the simplest Butler and Hopkins method and up to 0.50 for the Savitzky-Golay method. For the differentiation by Fourier Transformation a shape of filter (or weighting) function is very important, too.

"Differentiation is still rather a knack and not an automatic procedure", however, it could be helpful and powerful technique if skillfully used.

The above considerations are very important if the investigated spectrum consists of a number of bands with quite different halfwidths. Typical examples of such spectra are vibronic spectra of solutions.

ACKNOWLEDGMENTS

Valued discussions with Professor Adam Bartecki is kindly acknowledged.

REFERENCES

1. Maddams W.F.,Mead W.L. The Measurement of Derivative I.R. Spectra-I.Background Studies. Spectrochim. Acta 1982; 38A:437-444.
2. Hawkes S., Maddams W.F., Mead W.L., Southon M.J. The measurement of Derivative I.R. Spectra - II. Experimental Measurements. Spectrochim. Acta 1982; 38A: 445-458.
3. Griffiths T.R., King K., Hubbard H.V.St.A., Schwing-Weil M.-J., Meullemeestre J. Some Aspects of the Scope and Limitations of Derivative Spectroscopy. Anal. Chim. Acta 1982; 143: 163-176.
4. Gans P., Gill J.B. Examination of the Convolution Method for Numerical Smoothing and Differentiation of Spectroscopic Data in Theory and in Practice. Appl.Spectr. 1983; 37:515-520.
5. Gans P., Gill J.B. Smoothing and Differentiation of Spectroscopic Curves Using Spline Functions. Appl. Spectr. 1984; 38:370-376.
6. Cameron D.G., Moffatt D.J. A Generalized Approach to Derivative Spectroscopy. Appl.Spectr. 1987; 41: 539-544.
7. Savitzky A., Golay M.J.E. Smoothing and Differentiation of Data by Simplified Least Squares Procedures. Anal. Chem. 1964; 36:1627-1639.
8. Myrczek J. Computer Resolution and Franck-Condon Analysis of the Electronic Absorption Spectrum of $KMnO_4$ in Water. Spectr. Lett. 1987; 20: 927-944.
9. Bartecki A., Myrczek J.,Raczko M.,Cieślak-Golonka M. Computer Analysis of the Vibronic Spectra of $KCrO_3Cl$ in Acetone and Acetonitrile Solutions. Bull. Pol. Acad. Sci.: Chem. 1988; (in print).
10. Sowińska M., Myrczek J., Bartecki A. Vibronic Spectra of Chromium Compounds in Solutions. Proc. International School on Excited States of Transition Elements, Wrocław - Książ Castle, June 20-25, 1988, Poland.

11. Sowińska M.,Myrczek J., Bartecki A. Physicochemical Studies on Solid Products of Chromyl Chloride and Chromyl Acetate with Alkylaromatics. II. Electronic Absorption and Vibronic Spectra. (to be published).

Date Received: 09/13/88
Date Accepted: 10/18/88