ON THE NUMERICAL DESCRIPTION OF ASYMMETRIC ABSORPTION BANDS

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A procedure for analysing the asymmetry of smooth IR absorption bands, employing an asymmetric Cauchy-Gauss product function, is proposed. As an example the shape analysis of the ν_s(OH) absorption band of 2.4.6-trimethylphenol is presented.

Strictly symmetric absorption bands occur rarely in IR-spectroscopy. The asymmetry of most of well developed, smooth absorption bands is evident even in cases when the common source of this phenomenon, the overlapping of bands, is eliminated. The band asymmetry can be detected and analyzed by means of the method of moments [1, 2]. Some ways of handling asymmetric bands were pointed out by Pitha and Jones [3]. The resolution of such bands into two or more symmetric components, sometimes physically justified, often provides irreproducible or unacceptable results. The problem is also of importance in other spectroscopic methods.

For many purposes there is a need for an exact analytical expression describing the band shape. The only attempt to solve this problem for asymmetric bands was made by Cabana and Sandorfy [4] in a pure numerical way. Assuming that a single symmetric absorption curve can be described by means of a Cauchy (Lorentz) function,

$$A(\nu) = a_1(1+a_2^2(\nu-a_3)^2)^{-1} \tag{1}$$

where $A(\nu) = \lg\left(\frac{I_0}{I}\right)_\nu \left(\text{or } \ln\left(\frac{I_0}{I}\right)_\nu\right)$ is the shape function, ν is the wave number in cm^{-1}, a_1 is the peak height, a_3 is the band centre and $a_2 = \frac{1}{b}$ ($2b$ is the half-width of the band), these authors took the band asymmetry into account putting different b-values for the left and right part of the band (about the centre).

The aim of this work is to present another way for getting a numerical description of asymmetric bands, being in essence an extention of Cabana's and Sandorfy's idea. An

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individual symmetric absorption band cannot be exactly approximated by the Cauchy curve (1), nor by a Gauss function

$$A(\nu) = a_1 \exp\left(-a_4^2(\nu - a_3)^2\right) \tag{2}$$

where $a_4 = \frac{\sqrt{\ln 2}}{b}$. The best fit for symmetric bands can be achieved using the Cauchy-Gauss product function [3], [5]

$$A(\nu) = a_1(1 + a_2^2(\nu - a_3)^2)^{-1} \exp\left(-a_4^2(\nu - a_3)^2\right) \tag{3}$$

where a_1 and a_3 have the same meaning as before, and a_2, a_4 are shape parameters. If $\frac{a_2}{a_2 + a_4} \to 0$, the function (3) reduces to a Gauss curve, whereas if this factor tends towards unity, to a Cauchy curve. The half-width of the band, $2b$, can be found by a simple iterational procedure from a_1, a_2, a_4. Putting different shape parameters on each side of the band centre, a function providing for band asymmetry is obtained:

$$A(\nu) = a_1(1 + a_2^2(\nu - a_3)^2)^{-1} \exp\left(-a_4^2(\nu - a_3)^2\right)$$

$$\nu \leqslant a_3$$

$$A(\nu) = a_1(1 + a_5^2(\nu - a_3)^2)^{-1} \exp\left(-a_6^2(\nu - a_3)^2\right) \tag{4}$$

$$\nu > a_3$$

The peak height, a_1, and band centre, a_3, are common; the shape parameters are different on each side of the band: a_2, a_4 for $\nu \leqslant a_3$ and a_5, a_6 for $\nu > a_3$ (Fig. 1)

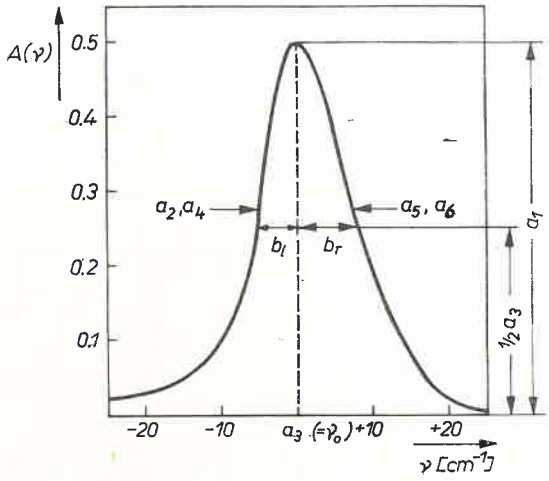

Fig. 1. Description of an asymmetric absorption band

If $a_2 = a_5$ and $a_4 = a_6$, the band is symmetric; if $L_l = L_r$, *i. e.* $\frac{a_2}{a_2 + a_4} = \frac{a_5}{a_5 + a_6}$, only the profile of both sides is identical.

Thus, using function (4), a single absorption band will be described by means of six parameters in place of three in the case of a Cauchy or Gauss curve, or four with the symmetric product function. For the evaluation of band parameters any of the optimization methods reviewed by Pitha and Jones [3] can be adapted. In this work programs based on the damped least squares iterational procedure were written [5].

In Table I a comparison of the numerical description of the OH-stretching vibration band of 2.4.6-trimethylphenol, using functions (1)–(4), is given; the best results are obtained with the asymmetric Cauchy-Gauss product (4). The transmission and wavenumber values,

TABLE I

Numerical description of the ν_s(OH) absorption band of 2.4.6-trimethylphenol at 3621.4 cm^{-1} (in CCl_4, 25°C, 22 exp. points, conc. = 2.216×10^{-3} mol/liter, spectral slit width $s = 2$ cm^{-1})

Function	Mean deviation	Root mean square deviation
Cauchy (Lorentz) (1)	0.0106	0.0133
Gauss (2)	0.0091	0.0133
Cauchy-Gauss symmetric (3)	0.0051	0.0088
Cauchy-Gauss asymmetric (4)	0.0020	0.0029

used in the calculations, were read from the spectrum; the use of a digital-output would further improve the fit between the experimental and calculated curves.

Using function (4), only a numerical description of an absorption band can be achieved. In a discussion of band asymmetry, the following quantities should be of interest: a) the asymmetry factor

$$k_{as} = \frac{\int_{-\infty}^{\nu_0} A(\nu)d\nu}{\int_{\nu_0}^{\infty} A(\nu)d\nu} = \frac{B_l}{B_r} \tag{5}$$

where B_l and B_r denote the intensities of the "left" and "right" parts of the band, respectively; b) the widths of these parts, b_l and b_r; c) the profile indices, L_1 and L_r, and the; statistical quantities [1], [2]:

$$\beta_l(j) = \frac{\mu_{4l}(j)}{\mu^2_{2l}(j)}\ ; \qquad \beta_r(j) = \frac{\mu_{4r}(j)}{\mu^2_{2r}(j)} \tag{6}$$

where $\mu_n(j)$ is the n-th truncated moment [1], [2] and $j = \frac{|\nu-\nu_0|}{b}$; $\mu_{n_l}(j)$ was calculated using a_2, a_4 and b_l, whereas for the evaluation of $\mu_{n_r}(j)$ a_5, a_6 and b_r were taken.

All quantities specified above can be easily calculated from the band parameters obtained by the least squares approximation. To check the repeatability of the procedure, a shape analysis of the ν_s(OH) absorption band of 2.4.6-trimethylphenol was performed. From the analysis of six spectra, recorded in the concentration range 1×10^{-3}—$5\times$ $\times10^{-3}$ mol/liter, the following results were obtained: $b_l = 5.9$ (±0.2) cm^{-1}, $b_r = 10.1$

($\pm$0.3) cm^{-1}, $k_{as} = 1.49$ ($\pm$0.06), $L_l = 84$ ($\pm$2)%, $L_r = 66$ ($\pm$1)%, $\beta_l(15) = 7.0$ ($\pm$0.6), $\beta_r(15) = 4.0$ ($\pm$0.2). It can be seen from the root mean square deviation values (given in parentheses) that the results are reproducible. It should be mentioned that the apparent band shape was analysed. The results were obtained for such low concentrations that association phenomena were eliminated; nevertheless, a considerable asymmetry of the band and profile differences of boths parts are revealed.

A precise analysis of asymmetry, using the above procedure, can be performed only on well outlined, single absorption bands. Programs for the resolution of multicomponent envelopes, simultaneously using asymmetric and symmetric curves, were also started during this work, but the results are not always satisfactory. In cases of strong overlap, the reliability of the calculated band indices is doubtful, although a very good fit between the experimental and "synthesized" envelopes can be achieved.

Experimental details. The spectra were recorded on a Unicam SP-700 spectrophotometer in the Central Laboratory of the Chemical Faculty of the Wrocław Technical University. The spectral slit width was exactly known (2 cm^{-1}). A pair of matched 10 mm "Infrasil" cells with teflon stopcocks was used. The samples were thermostated at 25$\pm$0.2°C. Density measurements of the solutions were carried out simulteneously (25$\pm$0.05°C). The spectra were recorded at a low scan rate to avoid the effect of mechanical and electronic distortion of the band profile, resulting in induced asymmetry [2]. The error caused by scattered radiation was negligible; no calibration of the intensity scale could be undertaken. The solvent used was CCl_4 (puriss.), fractionally distelled and dried over molecular sieves. 2.4.6-trimethylphenol (Fluka) was crystalized twice from benzene and stored in a vacuum dessicator over $MgSO_4$. The calculations were performed on Elliott 803b and Odra 1204 computers in the Wrocław University Computing Centre, following Mark III and Algol procedures.

REFERENCES

[1] R. N. Jones, K. S. Seshadri, N. B. W. Jonathan, J. W. Hopkins, *Canad. J. Chem.*, **41**, 750 (1963).
[2] K. S. Seshadri, R. N. Jones, *Spectrochim. Acta*, **19**, 1013 (1963).
[3] J. Pitha, R. N. Jones, *Canad. J. Chem.*, **44**, 3031 (1966).
[4] A. Cabana, C. Sandorfy, *Spectrochim. Acta*, **16**, 335 (1960).
[5] J. P. Hawranek, Wiadomości Chem., **24**, 225 (1970), (in Polish).