APPLICATION OF A GENERAL PROFILE FUNCTION
TO MATHEMATIC DESCRIPTION AND TO SEPARATION
OF BANDS IN THE INFRARED SPECTRUM
OF METHANESULPHONYL CHLORIDE*

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A new profile function[1] for simulating spectral band shapes was tested. Results of these tests both on theoretical curves (Cauchy, Gauss, and their products) and on experimental bands in the infrared spectrum of methanesulphonyl chloride (liquid or solutions) showed its considerable flexibility and its applicability in the description of infrared band profiles.

In various applications of spectroscopic methods, in particular when studying reasons of the broadening of spectral lines due to intermolecular interactions, it is necessary to simulate the shapes of experimental bands by analytical functions. The importance of these operations increases namely in the investigation of mutually overlapping bands, if their particular components should be separated mathematically. It was found experimentally that the shape of infrared absorption bands varies greatly, and thus the profile functions used so far have been of a limited applicability only. Therefore, this study aims at testing the possibility of using a more general function[1,2] of a larger versatility. Its flexibility was checked[3] by its ability to simulate the Gauss functions and the product Cauchy–Gauss function. In testing the new function on experimental bands all intense bands of the infrared spectra of methanesulphonyl-chloride over the wavenumber range $4000-600 \text{ cm}^{-1}$ and their satelites were subjected to simulation.

Method and Program Description

The experimentally observed course of absorbance in a spectrum can be mathematically approximated by the equation[4]

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$$A(\tilde{\nu}) = \alpha + \beta\tilde{\nu} + \gamma\tilde{\nu} + \sum_{j=1}^{N} A_j(\tilde{\nu}), \qquad (1)$$

where the polynomial approximates the background of the spectrum and $A_j(\tilde{\nu})$ each of the N profile functions used[4]; N is the number of bands. As an infrared band profile function most often the Cauchy function, the Gauss function as well as the product or the sum of both has been used. A general profile function which includes all the above mentioned types may be formulated as follows[1]

$$A^{(n)}(\tilde{\nu}) = A_{max}\Big[\sum_{i=0}^{n} p_i^2(\tilde{\nu} - \tilde{\nu}_{max})^{2i}\Big]^{-1}, \qquad (2)$$

where A_{max} and $\tilde{\nu}_{max}$ is the absorbance and the wavenumber of the band maximum, respectively, p_i are the shape parameters, and n is the quantity determining the function order.

To simulate the spectra, a computer program was written[3] which traces the contour of the experimental spectrum by function (1) using profile functions (2). The program optimizes the estimated parameters of the polynomial α, β, γ together with N sets of the parameters of all the profile functions $(A_{max}, \tilde{\nu}_{max}, p_1, p_2, \ldots p_n)$ by means of the Levenberg method of damped least squares[5,6]. It is very difficult to estimate from the recorded spectrum at once all parameters $p_1, p_2, \ldots, p_n$. Therefore, the algorithm of the program is so adjusted to consider first the first-order profile functions (2) which are identical with the Cauchy function. The parameter p_1 of this function can be rather easily estimated from the experimental spectrum, as it is simply related to the band half-width

$$p_1 = 2/(\Delta\tilde{\nu}_{1/2}). \qquad (3)$$

Iterative calculations specify all the parameters of the function in this order; only then the order of the profile functions n is increased by one. The higher-order parameters (p_n) are estimated as one tenth of the preceding parameter $(0.1\ p_{n-1})$.*

After optimizing the expanded parameter series using the above mentioned method, further increase of the profile function order is introduced *etc.* In this way the required profile function order can be obtained and good convergence properties of the algorithm can be kept at the same time.

The calculation was carried out in the units of absorbance (see equations (1) and (2)), with the exception of the sum of deviation squares, where the transmittance units were used; this was because the error is approximately constant in the transmittance scale[7,8] for both single-beam and double-beam instruments.

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* This relation was obtained empirically for liquids and solutions. It is not suitable to consider an estimation for $p_n = 0$ in view of the problems connected with the singularity of the set of normal equations.

RESULTS

The general profile function was used in describing the bands of methanesulphonyl-chloride (CH_3SO_2Cl) infrared spectrum. The spectrum of the liquid sample was investigated over the range $4000-600$ cm^{-1}, the spectrum of the solution in tetra-chloromethane over the range $2000-900$ cm^{-1}.

The calculations were carried out on a CDC 3300 computer using the above mentioned program in the USASI Fortran language.

The region $4000-600$ cm^{-1} of the liquid methanesulphonylchloride spectrum, containing nine intense bands, was approximated by a superposition of eleven profile functions (2) of the second or third order. The particular parameters are summarized in Table I. In the description of the solution spectrum over the region 2000 to 900 cm^{-1}, with five dominating bands, nine profile functions of the second or third order had to be used (Table II).

Figures 1 and 2 show the separations of the overlapping bands in the region 1500 to 1250 cm^{-1} for both the liquid and the solution.

The analysis of the regions containing overlapping bands enhances, after the separation, the possibility of the correct assignment of these bands. This can be shown, *e.g.*, in the analysis of the methanesulphonyl chloride spectrum between 1450 to 1250 cm^{-1}. In this region there lie the bands of bending vibrations of the CH_3 group

TABLE

Parameters ν_{max}, A_{max}, p_1, p_2, and p_3 of Functions (2), Background Parameters α and β of Function (*1*), and Standard Deviation σ of Bands in Liquid Methanesulphonyl Chloride Spectrum

Assignment	$\tilde{\nu}_{max}$ cm^{-1}	A_{max}	p_1 cm^2	p_2 cm^4	p_3 cm^6	α	β cm	σ % T
$\nu(CH)$	3 040·1	0·33	0·106	$0·197 . 10^{-3}$	$9·58 . 10^{-5}$	$-0·259$	$8·99 . 10^{-5}$	0·785
$\nu(CH)$	3 017·6	0·39	0·131	$7·141 . 10^{-4}$	$2·00 . 10^{-5}$			
$\nu(CH)$	2 932·4	0·45	0·154	$1·83 . 10^{-5}$	$1·48 . 10^{-5}$	$-0·751$	$2·62 . 10^{-4}$	0·413
$\delta(CH_3)$	1·410·0	0·07	0·146	$0·64 . 10^{-3}$	a			
$\delta(CH_3)$	1 375·7	0·28	0·098	$0·54 . 10^{-2}$	a			
$\nu_{as}(SO_2)$	1 364·4	0·56	0·087	$0·25 . 10^{-2}$	a	$-0·059$	$4·52 . 10^{-5}$	0·241
$\delta(CH_3)$	1 321·7	0·16	0·249	$1·69 . 10^{-2}$	a			
	1 176·7	0·40	0·130	0·00	a	2·61		0·529
$\nu_s(SO_2)$	1 170·2	0·43	0·159	$1·27 . 10^{-2}$	a			
$\varrho(CH_3)$	966·8	0·49	0·152	$1·05 . 10^{-2}$	$2·41 . 10^{-4}$	$-0·210$	$2·37 . 10^{-4}$	0·602
$\nu(CS)$	749·5	0·77	0·111	$1·07 . 10^{-2}$	$6·28 . 10^{-6}$	0·243	$-2·92 . 10^{-4}$	1·390

^{a} Calculations using function (2) in the second order only.

and the bands of antisymmetric stretching vibration of the SO_2 group of the molecule. Only the comparison of the results of separation of the liquid sample spectra and the CCl_4 solution spectra made it possible to assign the bands: the $v(SO_2)$ band is sensitive to environment effect, while the $v(CH_3)$ bands are practically not. An example of the spectra is in Fig. 1 and Fig. 2, the band assignment is shown in Table I and Table II. This detailed analysis of the methanesulphonyl chloride spectra under different conditions and their mathematical description made it possible to change somewhat the interpretation suggested recently by Nagel[9]; we differ from his results in several cases even in the values of band wavenumbers.

DISCUSSION

As shown earlier[3], functions (2) can be used to replace all basic profile functions used so far, as the Cauchy function (the general profile function of the first order is identical with it), the Gauss function, as well as the product Cauchy–Gauss functions. Function (2) used up to the third order offers in the simulation of these functions[3] values of the standard deviation within the limits of the experimental errors
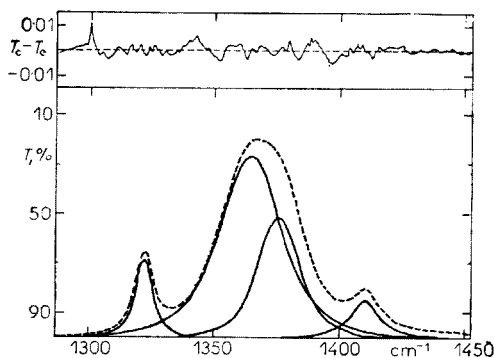

FIG. 1

Simulation of Liquid Methanesulphonyl Chloride Spectrum over the Region 1460 to 1270 cm^{-1}

Four profile functions (2) in the second order were used in the description (full curves), dashed curve — calculated spectrum envelope; upper part of the figure shows the course of the deviation of the calculated and experimentally measured spectrum envelope (10-times expanded scale); standard deviation, $\sigma = 0.241\% \, T$.
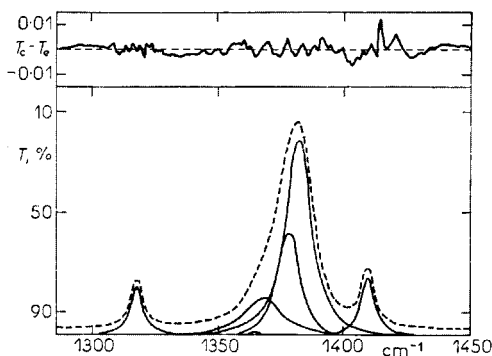
FIG. 2

Simulation of Methanesulphonyl Chloride Spectrum (solution in tetrachloromethane), Region 1460 − 1270 cm^{-1}

Six profile functions (2) in the second order were used in the description; details of the spectrum description as in Fig. 1, standard deviation, $\sigma = 0.174\% \, T$.

in the values of extinction of currently used commercial spectrophotometers[7]. The simulation of band profiles in experimental spectra of solution and liquid samples can be carried out with the help of function (2) in the second or maximally in the third order (cf. results in Table I and Table II). This fact is easily understandable, because intermolecular interactions lead to profiles similar to the Cauchy profile.

TABLE II

Parameters $\tilde{v}_{max}$, A_{max}, p_1, p_2, and p_3 of Functions (2), Parameters α and β of Function (1), and Standard Deviations σ of Bands in Methanesulphonyl Chloride Spectrum (solution in tetrachloromethane)

Assignment	$\tilde{v}_{max}$ cm^{-1}	A_{max}	p_1 cm^2	p_2 cm^4	p_3 cm^6	α	β cm	σ % T
$\delta(CH_3)$	1 409·5	0·12	0·337	$1·23 . 10^{-2}$	^{a}			
$v_{as}(SO_2)$	1 382·0	0·67	0·227	$8·19 . 10^{-3}$	^{a}			
$\delta(CH_3)$	1 378·1	0·23	0·171	$1·92 . 10^{-2}$	^{a}			
^{b}	1 368·2	0·07	0·122	$3·56 . 10^{-6}$	^{a}	$1·19 . 10^{-2}$		0·174
^{b}	1 364·9	0·01	0·355	$6·30 . 10^{-3}$	^{a}			
$\delta(CH_3)$	1 317·9	0·09	0·376	$8·27 . 10^{-4}$	^{a}			
$v_s(SO_2)$	$\begin{cases} 1\ 178·2 \\ 1\ 171·7 \end{cases}$	0·54 0·03	0·274 0·000	$0·47 . 10^{-3}$ $3·27 . 10^{-2}$	$0·00$ $2·07 . 10^{-3}$	$2·98 . 10^{-2}$		0·220
$v(CS)$	964·7	0·68	0·287	$1·10 . 10^{-2}$	$1·28 . 10^{-5}$	$1·04 . 10^{-3}$		0·495

^{a} Calculations using function (2) in the second order only; ^{b} bands not assigned.

TABLE III

Computing Times τ for Various Profile Functions

Profile function	τ μs
Cauchy	$(180 + 570\ N)\,p$
Gauss	$(180 + 1\ 300\ N)p$
Gauss–Cauchy (summ)	$(180 + 2\ 300\ N)p$
Gauss–Cauchy (product)	$(180 + 2\ 200\ N)\,p$
Function (2)	$[180 + (586 + 353n)\ N]\,p$

N number of bands; p number of experimental points; n order of function (2).

The application of function (2) in the description of profiles of infrared bands leads to a substantial improvement of the standard deviation of the experimental and the simulated spectrum as early as in the second or third order of function (2), often by as much as one order of magnitude.

In liquid and solution spectra there are sometimes bands whose center fits the Cauchy profile, while the wings fit the Gauss profile[8], function (2) can simulate even those composed profiles. However, a difficulty arises, if the superposition of symmetric functions is used to describe asymmetric bands: the physical interpretation of the results is then questionable. This case occurs in the absorption about $1\,173\,\mathrm{cm}^{-1}$ in the spectrum of methanesulphonyl chloride, where the experimental band can be described by two profile functions only (see bands 8 and 9 in Table II, assigned to the symmetric stretching $\nu(SO_2)$ vibration).

Another advantage of function (2) follows from its form: it requires considerably shorter computer time in comparison with the functions containing an exponential term. Experimentally determined values of computing times τ^* are shown in Table III.

It follows from the comparison of the computing times that function (2) of the second order requires computing times comparable to those of the simple Gauss function, and that it can compete with the product or sum Gauss–Cauchy function still in the fifth order. This advantage can be substantial in a numerical treatment of a large number of overlapping bands, *e.g.*, in high-resolution infrared spectra.

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* CPU computing time on computer IBM 360/40, PL/1 level F language, run under OS/360 Release 21·7 (MFT).