NEW FUNCTION DESCRIBING THE PROFILES OF IR ABSORPTION BANDS

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A new type of function describes profiles of IR bands especially for condensed phases. The proposed function is a generalization of the Cauchy (Lorentz) and Gauss functions.

For a long time, attention is paid to functions describing shapes of bands in the IR spectrum, especially of the condensed phases[1,2]. The analytical functions well approximating profiles of the individual spectral bands are needed not only for determination of integral intensities or separations of overlapping bands but also for the studies of physical phenomena causing their broadening.

THEORETICAL

The main factor governing the shape of IR absorption bands of liquids is the collision broadening process. Theoretical considerations based on a simplified model of collision processes[3] justify the use of the Cauchy (Lorentz) function, written *e.g.* in the form

$$A(\nu) = A_{\max} \cdot \left[1 + b_c^2(\nu - \nu_{\max})^2\right]^{-1} . \qquad (1)$$

It is often, however, realized that the simplified theoretical model does not offer good fit with the experimental data. The function (*1*) is therefore modified introducing Gaussian perturbations either by Voigt convolution[4] or using the Gauss product or sum functions[5-8]. The limiting cases represent bands with pure Gaussian profiles* expressed by the relation

$$A(\nu) = A_{\max} \cdot \exp\left[-b_g^2(\nu - \nu_{\max})^2\right] . \qquad (2)$$

The combinations of Cauchy and Gauss functions were successfully exploited in computerized separations of overlapping bands[8]. The increased number of parameters

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* Such a Gaussian curve is very suitable for description of electronic absorption bands but not of IR absorption bands of liquids.

resulted in a better fit between the calculated and experimental spectrum, on the other hand, however, the physical meaning of these parameters became vague. Moreover, the complexity of these functions causes numerical difficulties.

Let us define a new function $A(\nu)$ in the following way

$$A(\nu) = A_{\max} \cdot \left\{ \sum_{i=0}^{n} \frac{1}{i!} \left[b_i^2 (\nu - \nu_{\max})^2 \right]^i \right\}^{-1} . \qquad (3)$$

It is easy to see that both function (*1*) and function (*2*) are only two special cases of the function (*3*). The Cauchy (Lorentz) function is obtained by limiting the series (*3*) to the first two terms ($n = 1$ with $b_0 = b_1 = b_c$), the Gauss function requires $b_i = b_g = \text{const.}$ in the interval $i \in \langle 0, \infty \rangle$.

DISCUSSION

The proposed function (*3*) is a more flexible tool for description of the band profiles than the above mentioned ones. If b_i monotonously approaches to zero with increasing i, the curves lying between the Cauchy and Gauss functions are obtained (Fig. 1). If this condition is not fulfilled, the resulting curves have a markedly different character (Fig. 2). If $b_i = \text{const.}$, the function (*3*) with increasing n very rapidly converges to the Gauss curve; for $n = 5$ the difference between the function (*3*) and the Gauss function does not exceed $0{\cdot}01\ A_{\max}$ in the whole interval of ν.

The physical interpretation of the coefficients b_i is under study.

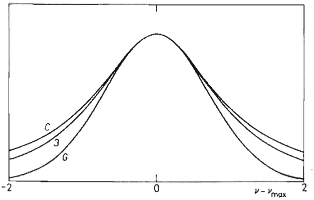

FIG. 1

A Comparison of the Cauchy Function, $b_c = 1{\cdot}0$ (*C*), the Gauss Function, $b_g = 1{\cdot}0$ (*G*) and the Function (*3*) for $n = 2$ Using the Coefficients $b_0 = b_1 = 1{\cdot}0$ and $b_2 = 0{\cdot}5$

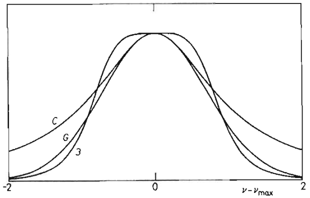

FIG. 2

A Comparison of the Cauchy Function, $b_c = 1{\cdot}0$ (*C*), the Gauss Function, $b_g = 1{\cdot}0$ (*G*), and the Function (*3*) for $n = 2$ Using the Coefficients $b_0 = 1{\cdot}0$, $b_1 = 0$ and $b_2 = \sqrt{2}$

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