

A re-examination of the line shape of the electronic spectra of complex molecules in solution: log-normal function versus gaussian[☆]

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Abstract

The log-normal function and the Gauss function have been tested for the description of highly structured UV/Vis spectra of complex molecules in solution. The Gauss function was shown to give the better fit for these spectra and is also useful for fluorescence spectra. These results were further supported by the application of the Ross function. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Electronic spectra; Log-normal function; Gaussian function; Line shape

1. Introduction

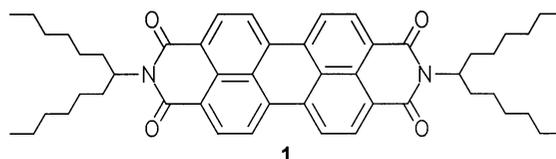
The log-normal function (Eq. (1)) has been suggested to be an appropriate description of the line shape of the electronic spectra of complex molecules in solution [1]. The function has been applied to rather broad absorption bands in the UV/Vis region. However, strongly structured UV/Vis spectra would give a better test for the line shape because deviations can be more easily detected and the function can be examined for each vibration band.

[☆] Dedicated to Prof. Dr R. Huisgen on the occasion of his 80th birthday.

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2. Experimental

The perylene-3,4:9,10-tetracarboxylic bisimide (**1** (S-13)) was prepared and purified according



to the literature [2]. A molar absorptivity of $88\,000\text{ l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ was obtained and the dye was free of coloured by-products according to thin-layer chromatography (silica gel/chloroform). Spectrograde solvents (Merck Uvasol[®]) were used for the measurements. UV/Vis absorption spectra were recorded by means of an OMEGA 20 spectrometer (Bruins Instruments, 0.25 m monochro-

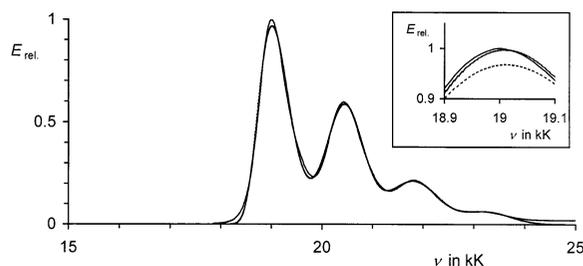


Fig. 1. UV/Vis absorption spectrum of compound **1** in chloroform (solid line) and the calculated spectrum from the log-normal function (Eq. (1)) (dotted line). Abscissa ν in $10\,000\text{ cm}^{-1}$ (kK). Ordinate $E_{\text{rel.}}$ in relative units. Insert: enlargement at $\nu_{\text{max.}}$; from top to bottom, absorption spectrum of compound **1** (solid line), Gauss function (Eq. (2)) (dashed line) and log-normal function (Eq. (1)) (dotted line).

mator) with a point separation of 0.2 nm, Fluorescence spectra were recorded with a 3000 spectrometer (Perkin Elmer), detected by an R 928 photomultiplier (Hamamatsu) and totally corrected according to Ref. [3]. The spectra were fitted by a simplex method according to Ref. [4].

Table 1

Optimized parameters for the simulated UV/Vis spectra of compound **1** (S-13) with the Gauss function (Eq. (2)) and the log-normal function (Eq. (1)), respectively

Gauss function			Log-normal function				
ν_{max} (kK)	$2\sigma^2$ (kK)	E_{max}	a (kK)	b (kK)	c	E_{max}	ν_0 (kK)
<i>Absorption</i>			<i>Absorption</i>				
24.26	0.777	0.019	17.57	1.50	0.210	0.989	18.2
23.35	0.252	0.044	7.24	13.21	-0.028	0.581	13.95
22.93	0.127	0.022	2.94	18.87	-0.026	0.212	12.52
21.80	0.526	0.212	3.14	20.14	0.023	0.059	13.06
20.44	0.268	0.586					
19.51	0.085	0.251					
19.00	0.123	0.985					
<i>Fluorescence</i>							
18.74	0.147	0.990					
18.20	0.082	0.180					
17.36	0.250	0.497					
16.07	0.420	0.111					
14.65	0.233	0.012					
13.33	1.246	0.006					

3. Results and discussion

The perylene-3,4:9,10-tetracarboxylic bisimide (**1**) [5] is a good probe for the investigation of the line shape of dyes because it exhibits a strongly structured UV/Vis absorption spectrum and a mirror-type fluorescence spectrum. The swallow-tail substituents of compound **1** at the nitrogen atoms renders the dye very soluble and lowers the tendency for aggregation. Chloroform as a solvent diminishes further this tendency. A fluorescence quantum yield of about 100% [3] also signifies that there is no aggregation in chloroform for concentrations of compound **1** which are suitable for optical measurements. Measurements of linear dichroism [6,7] indicate that essentially only one electronic transition is responsible for the absorption in the visible.

$$\varepsilon(\nu) = \frac{\varepsilon_0 b}{\nu - a} \exp(-c^2) \exp\left\{\frac{1}{2c^2} \left[\ln\left(\frac{\nu - a}{b}\right)\right]^2\right\} \quad (1)$$

The experimental spectrum of compound **1** has been fitted to a sum of the log-normal function (Eq. (1)) where $\varepsilon(\nu)$ is the absorptivity and ν the wave number. a , b , c and ε_0 are the parameters. ν_0

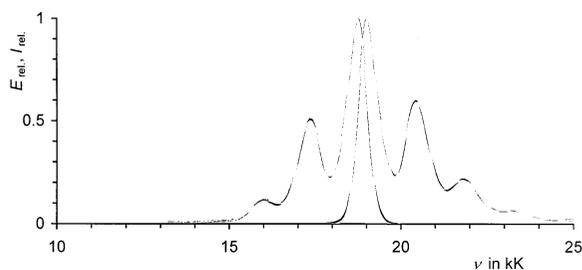


Fig. 2. UV/Vis absorption and fluorescence spectra of compound **1** in chloroform (solid line) and the calculated spectrum from the Gauss function (Eq. (2)) (gray line). Abscissa ν in $10\,000\text{ cm}^{-1}$ (kK). Ordinate $E_{\text{rel.}}, I_{\text{rel.}}$ in relative units.

is the position of the band and can be calculated from a , b and c according to Ref. [1]. ε_0 is the ε value at this position. The best fit of this sum of log-normal functions (Eq. (1)) to the UV/Vis absorption spectrum of compound **1** in chloroform is shown in Fig. 1. The parameters of the fit are given in Table 1. The log-normal function provides a reasonably good description of the spectrum (residue $R = 3.9\%$)¹ if one function is added for each maximum or point of inflection (number of vibration bands $n = 4$; this means 16 parameters). However, deviations from the spectrum are obtained where the spectrum is rather flat (see Fig. 1, insert).

$$\varepsilon(\nu) = \varepsilon_0 \exp\left[-\frac{(\nu - \nu_0)^2}{2\sigma^2}\right] \quad (2)$$

Alternatively, a sum of gaussian functions (Eq. (2)) has been fitted to the experimental spectrum of compound **1**. ε_0 , ν_0 and σ are the parameters. The best fit of the gaussian function (Eq. (2)) to UV/Vis absorption spectrum of compound **1** in chloroform is shown in Fig. 2. The parameters of the fit are given in Table 1. The result is an appreciably better fit to the experimental spectrum, even for the maxima and minima ($R = 1.7\%$) (see Fig. 1, insert). An additional Gauss function is needed between the first and the second vibration band so that five Gauss functions are required for the spectrum according to Fig. 1;

two additional Gauss functions are calculated for the region at shorter wavelengths (see Fig. 2 and Table 1). However, despite this extra band, an economy of parameters is given for the Gauss function because each log-normal function needs four parameters, whereas the Gauss function needs only three. Moreover, the Gauss function also fits for the fluorescence spectrum of compound **1** (see Fig. 2).

$$I_n/I_0 = (\nu_n/\nu_0)x^{2n}/n! \quad (3)$$

The analysis of the intensities of the vibration bands yields a further support for the use of the Gauss function. A good approach for intensities is given by the Ross function [8] (Eq. (3)), where n is the quantum number of the vibronic excitation and x a measure for the distortion between the ground and the excited state. I is the intensity of the transition and ν the wavenumber. The ε values of Table 1 have been normalized and taken as a measure for the I values of Eq. (3). An application of Eq. (3) to the intensities obtained by the log-normal function (Eq. (1)) does not give good results. However, a good fit is obtained for the intensities from the Gauss functions (Eq. (2)) and $x = 0.745$ for both the absorption and fluorescence spectra. This is shown in Fig. 3. An exception to this is the second Gauss band in absorption and fluorescence. These bands seem to have some other origin than the normal vibration bands. A further indicator of this is the fact that the latter are nearly equidistant with $\Delta\nu$ about 1350 cm^{-1} , whereas the former do not fit this order. Interestingly, the separation of these extra

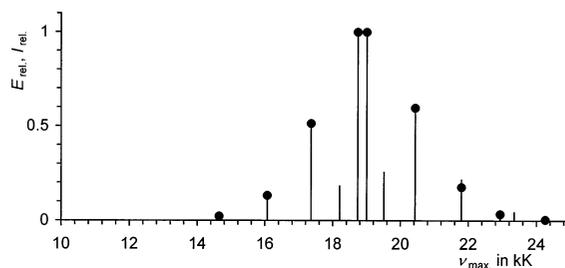


Fig. 3. Line positions and intensities of the UV/Vis absorption and fluorescence spectra of compound **1** obtained by the Gauss analysis according to Fig. 2 (bars), and the calculated intensities by the Ross function (Eq. (3)) (circles).

¹ $R = \sqrt{\int [\varepsilon(\nu)_{\text{calcd.}} - \varepsilon(\nu)_{\text{exp}}]^2 d\nu / \int [\varepsilon(\nu)_{\text{exp}}]^2 d\nu}$.

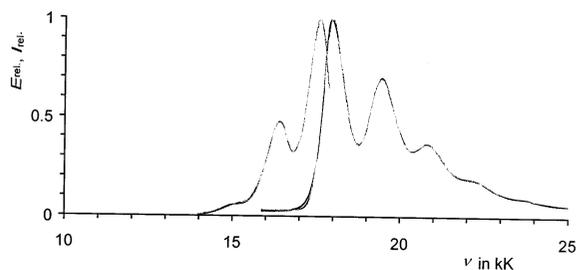


Fig. 4. UV/Vis absorption and fluorescence spectra of terrylene in chloroform (solid line) and the calculated spectrum from the Gauss function (Eq. (2)) (gray line). Abscissa ν in $10\,000\text{ cm}^{-1}$ (kK). Ordinate $E_{\text{rel.}}, I_{\text{rel.}}$ in relative units.

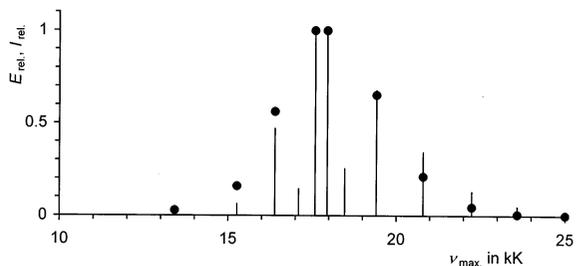


Fig. 5. Line positions and intensities of the UV/Vis absorption and fluorescence spectra of terrylene obtained by the Gauss analysis according to Fig. 4 (bars), and the calculated intensities by the Ross function (Eq. (3)) (circles).

bands in absorption and fluorescence is also about 1350 cm^{-1} .

The good fit of structured UV/Vis spectra by a gaussian line shape is not a special case for compound **1**, but can be also applied other spectra. For example, a Gauss analysis is demonstrated for terrylene in Fig. 4. The vibration structure thus obtained is very similar to compound **1** (see Fig. 5). This vibronic structure can be also verified by Eq. (3) with $x = 0.777$ (some deviations may have their origin in the

instability of terrylene, which makes the precise recording of UV/Vis spectra difficult).

4. Conclusion

A gaussian line shape seems to be the most appropriate description for structured UV/Vis spectra. However, it must be pointed out that this concerns only monodispersal dissolved dyes, whereas lorentzian line shapes are typical for aggregates [9]. An analysis of the line shape of the spectral edge of UV/Vis spectra at long wavelengths [10] also favoured gaussian type functions.

Acknowledgements

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