

# Determination of the Overlap Between UV Absorption Spectrum and Fluorescence Spectrum

Heinz Langhals

Chemisches Laboratorium der Universität Freiburg, Albertstr. 21, D-79104 Freiburg i.Br. (R.F.A.).  
Presently: LMU University of Munich, Department of Chemistry, Butenandtstr. 13,  
D-81377 Munich, Germany,  
E-Mail: Langhals@lrz.uni-muenchen.de.

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A new and simple method for determining overlap of electronic and fluorescence spectra is described. Two quantities, spectrum separation ( $ST$ ) and the separation figure ( $TZ$ ), are derived by a tangent method; for some applications, they offer a better description of overlap of absorption and fluorescence spectra than the commonly used Stokes' shift.

Ein neues, einfaches Verfahren zur Bestimmung der Überlappung zwischen Elektronen- und Fluoreszenzspektrum wird beschrieben. Mit der hier abgeleiteten Spektrentrennung  $ST$  und der Trennzahl  $TZ$  werden zwei Größen erhalten, die die Überlappung zwischen Absorptions- und Fluoreszenzspektrum beschreiben. Die nach einer Tangentenmethode bestimmten Größen beschreiben für einige Anwendungen die Überlappung besser als der bisher benutzte Stokes-Shift.

Fluorescent dyes are of considerable importance in many areas of chemistry and technology. Of particular note are recent developments in which fluorescent dyes find use in fluorescent collectors for solar energy harvesting [1] and energy conversion in general [2]. In contrast, however, few quantities are currently available to characterize the properties of these dyes. For application as laser dyes, in scintillators and fluorescence collectors, it is of particular importance that absorption and fluorescence spectra are as well separated as possible. The overlap of both spectra should be as small as possible. In connection with the development of fluorescent dyes for solar collectors, a method was therefore developed to quantitatively measure the overlap of the spectra.

To characterize absorption and fluorescence spectra, the Stokes' shift is often used [3], as the frequency difference of the maximum extinction coefficient and the fluorescence intensity, or as the frequency difference of the band centroids. The spectral overlap is inadequately described in this case because the Stokes' shift depends strongly on the band shape, while the overlap is given by the overlap integral of the spectra. However, since the extinction coefficient and the fluorescence intensity have different dimensions, a direct numerical comparison of the overlap integral with, for example, the absorption spectrum is not possible. An arbitrary factor is needed to fit the fluorescence spectrum to the absorption spectrum.

These difficulties can be easily circumvented with the method described in this paper.

It is assumed that both the absorption and fluorescence spectra can be represented as a superposition of Gaussian functions (abscissa in energy scale e.g. wavenumber  $\tilde{\nu}$ ), a common approach in the analysis of UV spectra [4,5]. The method described in the literature [5] of determining the partial bands of the spectra by a Gaussian analysis presents some problems. For example, the number of partial bands must be known for an accurate analysis. Moreover, the actual analysis represents a multiparameter fit with the known problems, among other things, of secondary minima. Therefore, the result is likely to have considerable uncertainties, especially for poorly structured spectra.

## Results

The new method described here eliminates the difficulties of the previous analyses and is also very easy to perform. It is also based on the assumption that the spectra are composed of Gaussian functions (this assumption should be quite well satisfied in most cases). In particular, this will be true for the longest wavelength absorption and shortest wavelength fluorescence bands. The long-wavelength slope of the absorption spectrum and the short-wavelength slope of the fluorescence spectrum are then, to a very good approximation, branches of Gaussian functions. The next long-wavelength or short-wavelength partial band has already decayed so much in the branches that it is no longer of appreciable importance (exponential decay of the band). This will be the more precise the more structured the spectrum is, but even with little structured bands there will not be too much deviation. With the help of the special properties of

the Gaussian function, it is now possible to determine the last partial band of each spectrum from the long-wave or short-wave branches without having to consider the others.

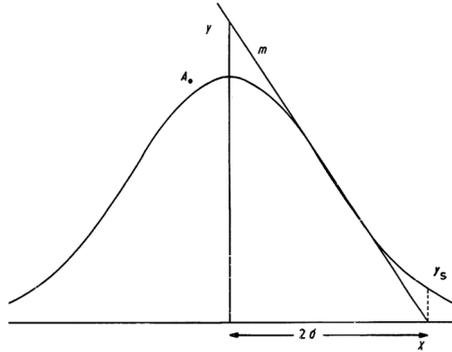


Figure 1. Gaussian function with turning tangent

For the Gaussian function  $y = A_0 \cdot \exp[-x^2/(2\sigma^2)]$  according to Fig. 1, the points of inflection are at  $\pm\sigma$ , the point of intersection of the inflection tangents with the  $x$ -axis is at  $\pm 2\sigma$ . The slope of the turning tangents is:

$$m = \pm (A_0/\sigma) \exp(-1/2). \quad (1)$$

The function value of the Gaussian function  $y_s$  at the intersection of the tangents with the  $x$ -axis is:

$$y_s = A_0 \cdot \exp(-2). \quad (2)$$

From Equations (1) and (2), the variance  $\sigma$  can be calculated:

$$\sigma = \pm(y_s/m) \exp(1.5). \quad (3)$$

It then allows to determine the position of the longest wavelength partial band in the UV spectrum. The process is described here using the example of absorption and can be carried out in a mirror image for fluorescence.

The turning tangent is applied to the long-wavelengths flank of the absorption spectrum (schematically according to Fig. 2). This can be done visually, with a mirror ruler or with a computer by differentiating twice.

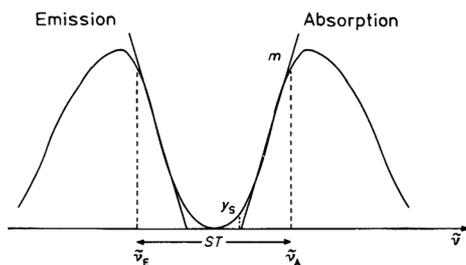


Figure 2. Application of the tangent method

The slope  $m$  of the tangent is determined and the extinction value  $y_s$  at the intersection of the tangent with the  $x$ -axis. The variance  $\sigma$  is calculated according to Equation (3). The maximum of the longest wavelength partial band must then lie  $2\sigma$  from the intersection of the turning tangents with the abscissa to shorter wavelengths. Analogous procedure is used for the fluorescence spectrum - here the partial band at shortest waves.

For the properties of fluorescent dyes, it is important how far apart are the described partial bands of the absorption and fluorescence spectrum. The spectrum separation  $ST$  is defined as the wavenumber difference  $\tilde{\nu}_A - \tilde{\nu}_F$  of the two partial bands. It is given for some dyes in Table 1.

With the calculated values of  $\sigma$  and  $\tilde{\nu}_{\text{Max}}$  for the absorption and fluorescence spectra, the overlap integral of the last partial bands of both spectra can be calculated: The essential contribution of the overlap. The overlap integral is assumed to be:

$$S = \int_{-\infty}^{+\infty} A_{0A} \exp[-(\tilde{\nu} - \tilde{\nu}_A)^2/(2\sigma_A^2)] \cdot A_{0F} \exp[-(\tilde{\nu} - \tilde{\nu}_F)^2/(2\sigma_F^2)] d\tilde{\nu} \quad (4)$$

With  $ST = \tilde{\nu}_A - \tilde{\nu}_F$  it follows:

$$S = A_{0A} A_{0F} \cdot \sqrt{\frac{2\pi\sigma_A^2 \cdot \sigma_F^2}{\sigma_A^2 + \sigma_F^2}} \cdot \exp[-ST^2/(2(\sigma_A^2 + \sigma_F^2))] \quad (5)$$

As can be seen from Equation (5),  $S$  consists of a constant  $\sqrt{\pi}$ , an amplitude factor  $A_{0A} \cdot A_{0F}$ , the square root of the harmonic mean of the squared variances of the absorption and fluorescence spectra, and an exponential factor  $\exp[-ST^2/(2(\sigma_A^2 + \sigma_F^2))]$ . It can be seen that when the spectral separation  $ST$  is sufficiently large, the exponential factor has the greatest effect on the overlap integral  $S$ . Therefore, it can be considered as a measure of  $S$  (the other influences enter  $S$  only linearly). To quantify the influence of this exponential factor, it is convenient to define the separation number  $TZ$ .

$$TZ = \exp[ST^2/(2(\sigma_A^2 + \sigma_F^2))] \quad (6)$$

$TZ$  is a good measure of  $S$  and can take values from 1 to  $+\infty$  as a dimensionless number and increases with increasing spectral separation (decreasing  $S$ ).

### Discussion of the results

In order to check to what extent, the assumption is fulfilled for experimental spectra that the falling edges of the spectra represent branches of Gaussian functions,  $\ln \varepsilon$  was plotted against  $(\tilde{\nu} - \tilde{\nu}_A)^2$  in Fig.

Table 1. Analysis of UV absorption spectra and fluorescence spectra according to the tangent method

Dye <sup>a)</sup>	$\tilde{\nu}_A$ <sup>b)</sup>	$\sigma_A$ <sup>c)</sup>	$\tilde{\nu}_F$ <sup>b)</sup>	$\sigma_F$ <sup>c)</sup>	$ST$ <sup>d)</sup>	$TZ$ <sup>d)</sup>	Ref. <sup>e)</sup>
Rubrene	18690	331	18050	461	634	1.9	374
Fluorescein	19610	366	18810	389	803	3.1	410
Octamethylbiphenyl	35950	497	34980	355	969	3.5	184
Acridine yellow	21620	594	20310	463	1310	4.6	407
Rhodamine B	18020	399	16840	447	1180	6.9	411
Esculin	28730	1060	25720	760	3010	14.5	328
4-(3,3-Dimethylbutoxy)- <i>p</i> -terphenyl <sup>f)</sup>	33040	1290	29350	559	3690	31.9	227
4-(3,3-Dimethylbutoxy)- <i>p</i> -terphenyl <sup>g)</sup>	33640	1520	29300	632	4340	32.6	226
4-Methoxybiphenyl	36520	1361	31470	677	5050	249	185
Quinine hydrogensulfate	28130	1100	22920	1040	5210	385	406
4,4'-Di-isobutoxybiphenyl	35930	1440	30080	709	5850	787	192
Benzidine	33670	1510	25450	1180	8220	10100	193

a) All data except  $TZ$  in  $\text{cm}^{-1}$ . - b) Position of the longest and shortest wavelength partial bands in the absorption and fluorescence spectra. - c) The variances belonging to b). - d) See text. - e) Page number according to Ref. [6]. - f) Measured in benzene. - g) Measured in ethanol.

3 for an example ( $\tilde{\nu}_A$  was determined according to the tangent method). For the branch of a Gaussian function a linear relation should result. According to Fig. 3 this condition is fulfilled very well. The variance  $\sigma_A$  determined from the slope of the straight line agrees within 5% with the variance determined according to the tangent method (Table 1).

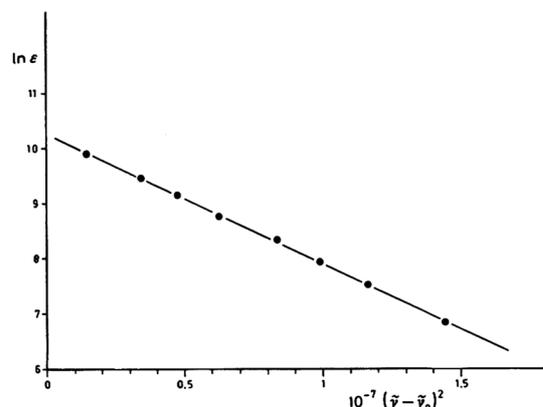


Figure 3. Linear relationship of  $\ln \epsilon$  versus  $(\tilde{\nu} - \tilde{\nu}_A)^2$  of 4-(3,3-dimethylbutoxy)-*p*-terphenyl in ethanol.  $\tilde{\nu}_A$  see Table 1.

Table 1 gives the separation number  $TZ$  for a series of fluorescent dyes taken from Ref. [6]. It can be seen that the value of  $TZ$  parallels the visual impression of spectral overlap.

With the quantities  $ST$  and  $TZ$  defined in this work, it is possible to describe important properties of fluorescent dyes in a compressed way. In addition, they can be used to quantitatively investigate other effects such as the solvation of 4-(3,3-di-methylbutoxy)-*p*-terphenyl (Table 1).

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