

The Effect of Unequal Davidoff (Exciton) Linewidths on the Quantum Yield of the Photoproducts of Asymmetric Bichromophoric Molecules

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A bichromophoric molecule is asymmetric in the sense of having two chromophores of different energies for their first excited states, prior to the ‘application’ of the Davidoff (exciton) interaction. The quantum yield of the photoproducts is considered for the case in which the two Davidoff lines are Gaussian. Particular attention is paid to the effect of differences in the width of the two lines, and the theory is compared with experimental results on bilirubin.

1. Introduction

We here summarise a complete theory of the dependence of quantum yield on wavelength in the case of Gaussian lines, and in particular discuss the effect of differences in the widths of the lines. Information on the linewidths and the amplitudes provides material from which deductions may be made concerning the dihedral angle between the chromophores of a bichromophoric molecule [1]. We analyse in particular data on bilirubin.

Let the two energies be E_i and E_j and let the Davidoff (exciton) parameter be $2V_{ij}$. The ratio $2V_{ij}/(E_i - E_j)$ is supposed independent of wavelength. Then the quantum yield of the products has been shown [2] to be proportional to $\{c^2 I_\beta(\lambda) + s^2 I_\alpha(\lambda)\} / \{I_\beta(\lambda) + I_\alpha(\lambda)\}$, where $I_\beta(\lambda)$ and $I_\alpha(\lambda)$ give the shape of the lines, λ is the wavelength and c^2 and s^2 denote the probabilities that the j chromophore state occupies the β and the α Davidoff states respectively. Note that $c^2 + s^2 = 1$ and that these quantities are taken to be independent of λ .

2. Mathematical Analysis

We can write for the two Gaussians:

$$I_\beta(\lambda) = A_1 \exp\left(-\frac{(\lambda - \lambda_1)^2}{2\sigma_1^2}\right) \quad I_\alpha(\lambda) = A_2 \exp\left(-\frac{(\lambda - \lambda_2)^2}{2\sigma_2^2}\right)$$

The convention shall be that the labels β and 1 apply to the line with the lesser central point: $\lambda_1 < \lambda_2$. We may choose a vertical scale for which $A_1 = 1$ and $A_2 = k$. We may also scale the horizontal axis, putting

$$\frac{1}{2\sigma_1^2} = S^{-2} a^{-2} (1 + \varepsilon), \quad \frac{1}{2\sigma_2^2} = S^{-2} a^{-2} (1 - \varepsilon),$$

where S is a dimensionless scale-factor. Initially it will be assumed that $\varepsilon \neq 0$; the case $\varepsilon = 0$ will be dealt with later, briefly and separately. We may also choose the origin of λ in such a way that $\lambda_1 + \lambda_2 = 0$. That is to say: $\lambda_1 = -Sa$, $\lambda_2 = +Sa$, where a is positive, by the convention just adopted. Write $\lambda = Sx$.

We thus have:

$$I_\beta(\lambda) = \exp(-(1 + \varepsilon)(x + a)^2 a^{-2}) \quad I_\alpha(\lambda) = k \exp(-(1 - \varepsilon)(x - a)^2 a^{-2}).$$

All this is perfectly general. It is merely the choice of a standard form. Now consider the quantum yield:

$$\Theta = \frac{c^2 I_\beta + s^2 I_\alpha}{I_\beta + I_\alpha}$$

By application of standard calculus techniques the shape of the graph of Θ as a function of x may be derived. We here summarise the results. The case in point will be that in which the β line is the wider (i.e. $\varepsilon < 0$) and $c^2 > s^2$, as this applies to the data-set we have analysed. Other cases are similar, and may be similarly described, *mutatis mutandis*.

As $x \rightarrow \pm\infty$, $\Theta \rightarrow c^2$, and this is its maximum value. The minimum value is achieved when $x = a/\varepsilon$, and the graph is symmetric about this; if ε is even only very slightly less than 1, then that minimum will be extremely close to s^2 . The slope of the graph at the level $\Theta = \frac{1}{2}$ is given by $\left| \frac{d\Theta}{dx} \right| = a(c^2 - s^2)$, so that the steepness of the sides of the “well” is directly proportional to a .

However, in the degenerate case $\varepsilon = 0$, the asymptotic values are c^2 to the left and s^2 to the right and the graph is monotonic decreasing.

3. Experimental Results

We earlier [3] reported results obtained for bilirubin 4Z-15Z-IX α in NH₄OH/MeOH. The fit of the two Gaussians gave, in the new scaled co-ordinates, $a = 1.09$, $\varepsilon = -0.532$, $k = 1.387$, $S = 0.0326$. The fit was recalculated but this time with the widths constrained to be equal, and so only five parameters were estimated. This resulted in the scaled parameters: $a = 0.515$, $\varepsilon = 0$, $k = 0.545$, $S = 0.0224$.

The scaled values of x ran from -3.08 to $+3.44$ in the first case, and from -2.13 to $+2.35$ in the second. From separate data [3], the value of c^2 was estimated as 0.59.

The graphs below show the variation of Θ with λ in both cases. They are comparable, but the second has a gentler slope by virtue of the smaller value of a , nor does it exhibit the upturn to the right of the diagram.

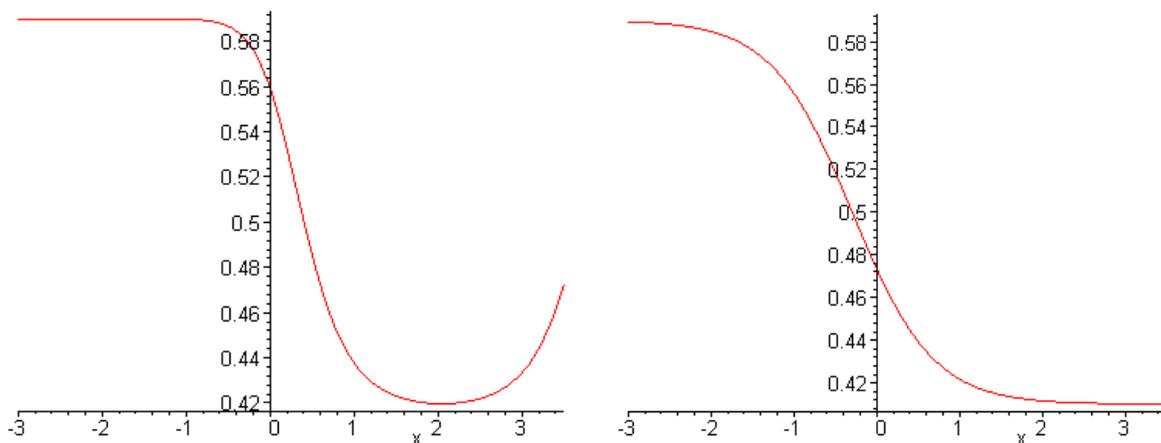


Figure 1. Plot of Quantum Yield against Wavelength;
Left: Case of Unequal Linewidths; Right: Case of Equal Linewidths

The question of which choice gives the better model may be addressed by the use of an *F*-test. Bates and Watts [4] recommend this procedure generally, when it comes to choosing between models with different numbers of assignable parameters. Here it is particularly apt,

as it is *precisely* the question of equality of variances which is in point, and this is what the *F*-test was specifically designed to test.. Bates and Watts' statistic s_e^2/s_f^2 for the data, covering 200 values of λ , as calculated from the fitting procedure, was found to be 134.75, greatly in excess of the relevant value of $F(1, 194; 0.01)$ (= 2.4), so the inclusion of the extra parameter ε is overwhelmingly justified.

The estimate of the dihedral angle in the bilirubin molecule depends on which model is adopted. The general formula for this angle is $\vartheta = 2 \tan^{-1} \sqrt{k \sqrt{\frac{1+\varepsilon}{1-\varepsilon}}}$ which gives 82.4° in the general case, but 72.9° from the constrained fit. This last is the value calculated by Mazzoni *et al* [5] who used the constrained model. The use of the general case (as opposed to what is, after all, a degenerate subcase) produces a difference of over 11% in this estimate. While it is good methodology to analyse the simpler model first, the more detailed analysis leading to the inclusion of the extra parameter ε provides a more accurate fit and the statistical test amply justifies the added complication.

4. Further Remarks

The fits of the sums of Gaussians were derived from a computer-assisted (EXCEL) search over the whole of the relevant region of parameter-space. Thus we have avoided many of the perils that such fits can involve [4, 6] and can be confident that the parameter-values given are those that truly minimise the sum of the squared errors. Nonetheless it should be noted that the ill-conditioning that besets such fits is still a factor to be considered. Although the r^2 values are impressive (99.87% for the general case, and 99.25% for the constrained), the large discrepancies in the parameter-estimates, especially in the case of k , urge caution. The difficulty remains even though the dataset from which the fits were derived is highly accurate, and covers the relevant range of λ . The values of c^2 and s^2 used in the text are not known with great accuracy, but they suffice for illustrative purposes.

The difference in the linewidths is nonetheless conclusively demonstrated. The use of equal linewidths has been promoted by the work of Lightner *et al.* [7] who used the approximation of equal excited state energies for the two chromophores with some success. However, the equal energy solution is a special case of the quantum mechanical problem. The underlying reason for the difference in linewidths may lie either in the interactions between the two chromophores or else between the chromophores and the solvent.

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