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A Study on the Relationship Between Stoke's Shift and Low Frequency Half-value Component of Fluorescent Compounds

Xuhong Qian,* Yulan Zhang, Kongchang Chen, Zhifu Tao & Youngjia Shen

P.O. Box 544, 130 Meilong Road, East China University of Science and Technology, Shanghai 200237, People's Republic of China

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ABSTRACT

*Pestemer's rule on the relationship between the difference in absorption in solution and fluorescence on fiber substrate and low frequency half-value component (*H*) was demonstrated and developed to study the relationship between the Stoke's shift in solution and the low frequency half-value component. The following equation was established:* Stoke's shift $= 2kH + b$ cm^{-1}, *where* k *is greater than 2 and* b *is a constant. Examples are given on the experimental correlation between Stoke's shifts and the low frequency half-value components of naphthalimide dyes, DNA intercalative dyes and benzoxazole dyes. Copyright © 1996 Elsevier Science Ltd*

Keywords: Stoke's shift, low frequency half-value component, fluorescent compounds, relationship, absorption, fluorescence.

INTRODUCTION

We have previously found that there was a good linear relationship (with slope 1) between the maximal wavenumbers of absorption and fluorescence of benzoxanthene-3,4-dicarboximide dyes in dimethylformamide solution.[1] Other researchers have theoretically predicted both the maximal wavenumber of absorption and of fluorescence of laser dyes based on a linear correlation equation, in which the only variable used is the excitation energy

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*To whom correspondence should be addressed.

calculated by the HMO method.[2,3] These results can be explained using Pestemer's rule.[4,5]

According to the investigations carried out by Pestemer *et al.*,[4] there is a distinct relationship between the position and shape of the characteristic maxima of fluorescent brightening agents and fluorescent dyes with respect to the UV absorption in solution (water, methanol, dimethylformamide) and the fluorescence on a fiber substrate (cotton, polyester, acetate filament, polyamide). Neglecting a wide variety of influences on the absorption and fluorescence band, sufficient proportionality exists between the difference in the absorption and fluorescence maxima (cm^{-1}) and the low-frequency half-value component H (cm^{-1}), as described by eqn (1).

$$V^{\mathrm{uv}}_{\mathrm{max}}(\text{in solution}) - V^{\mathrm{fl}}_{\mathrm{max}}(\text{on substrate}) = 2.5H(\mathrm{cm}^{-1}) \qquad (1)$$

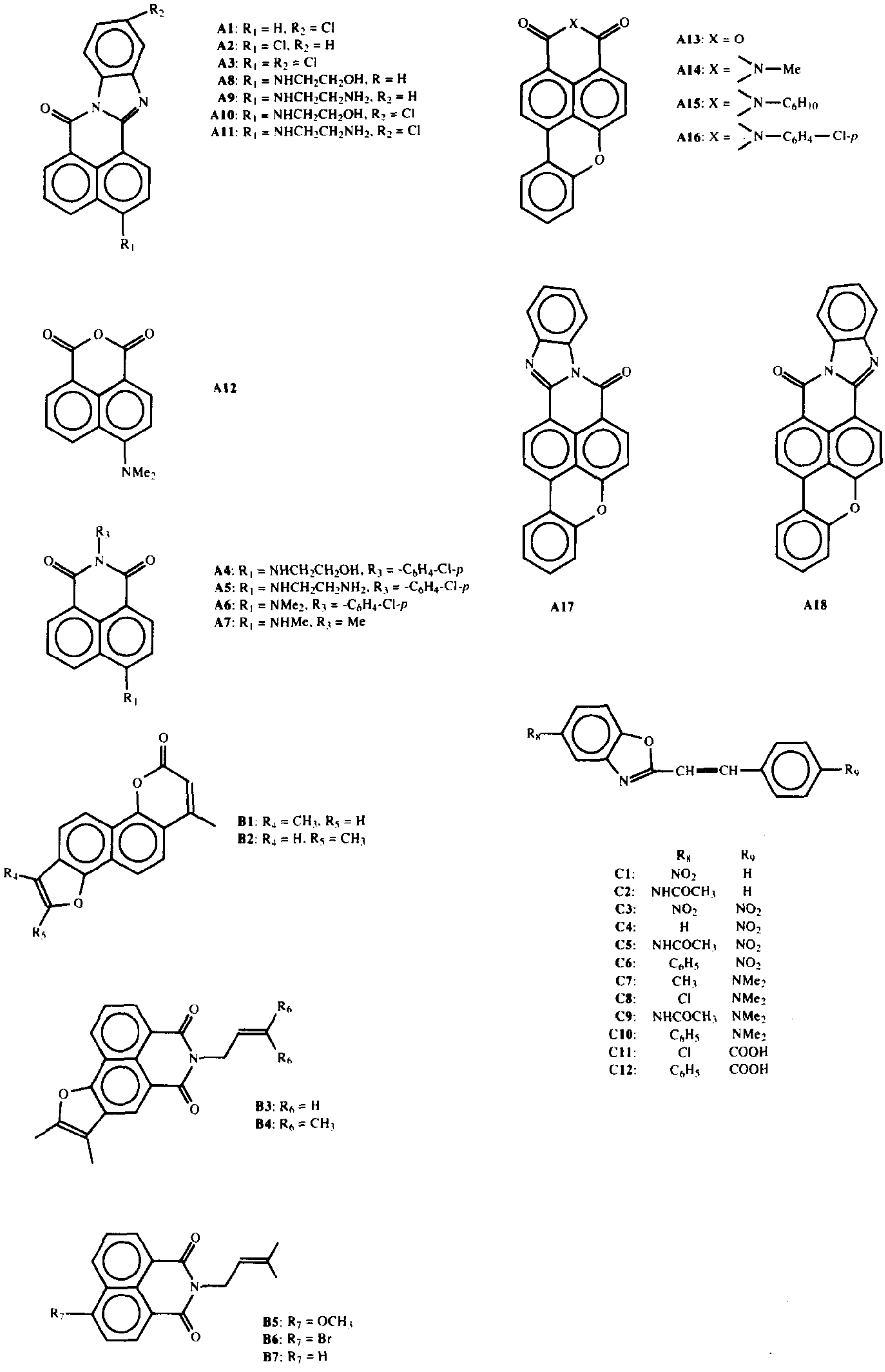
It is known that in dye solutions of low concentration the half-band width determined experimentally at half height of the absorption peak is often used to judge the color purity or brightness of a dye. For a series of analogous ones, it is thus possible to predict the brightness through the calculation of H, if the shape of their absorption peaks are presumed to be approximately similar.

We were interested in Pestemer's rule with respect to considering whether a similar linear relationship existed between the difference in the absorption and fluoresence maxima values in the same solution (Stoke's shift) and their low frequency half-value component, and if so, whether the coefficient for H was also equal to 2.5; and whether it could then be used as a basis to theoretically calculate or predict the value of H or Stoke's shift.

In this paper, we demonstrate the general relationship between Stoke's shifts and low frequency half-value components of fluorescent compounds, and report their experimental correlation for naphthalimide dyes, DNA intercalative dyes and benzoxazole dyes.

EXPERIMENTAL

The syntheses of all compounds used has been reported previously;[6–10] their structures are shown in Fig. 1. Fluorescence and absorption spectra were recorded in dimethylformamide or ethanol on a Shimadzu UV-265 and a Hitachi 850 fluorescence spectrometer, respectively. Relevant absorption and fluorescence maxima wavenumbers, as well as the low frequency half-value components on absorption thus determined, are listed in Table 1.[8–10]



	R$_8$	R$_9$
C1:	NO$_2$	H
C2:	NHCOCH$_3$	H
C3:	NO$_2$	NO$_2$
C4:	H	NO$_2$
C5:	NHCOCH$_3$	NO$_2$
C6:	C$_6$H$_5$	NO$_2$
C7:	CH$_3$	NMe$_2$
C8:	Cl	NMe$_2$
C9:	NHCOCH$_3$	NMe$_2$
C10:	C$_6$H$_5$	NMe$_2$
C11:	Cl	COOH
C12:	C$_6$H$_5$	COOH

Fig. 1. Structures of fluorescent naphthalimide dyes **A1–A18**, DNA intercalative dyes **B1–B6** and benzoxalo dyes **C1–C12**.

TABLE 1
Stoke's Shifts and Low Frequency Half-value Components of Compounds*

Compound	Stoke's shift (k cm^{-1})	H (k cm^{-1})	Compound	Stoke's shift (k cm^{-1})	H (k cm^{-1})
A1	4.30	2.59	**A10**	2.54	1.81
A2	6.03	3.17	**A11**	2.29	1.92
A3	5.89	2.83	**A12**	4.30	2.23
A4	3.80	1.95	**A13**	2.41	1.82
A5	3.72	2.10	**A14**	2.30	1.88
A6	4.28	2.35	**A15**	2.40	1.74
A7	3.61	1.85	**A16**	2.49	1.82
A8	2.09	1.64	**A17**	2.07	1.69
A9	2.11	1.65	**A18**	2.01	1.52
B1	3.00	1.23	**B5**	4.83	1.91
B2	3.10	0.89	**B6**	3.95	1.88
B3	8.47	2.83	**B7**	2.75	1.48
B4	8.26	3.35			
C1	6.75	2.94	**C7**	4.99	2.02
C2	5.72	2.07	**C8**	4.92	1.82
C3	2.81	1.32	**C9**	4.87	2.10
C4	4.41	2.22	**C10**	4.83	1.87
C5	2.91	1.40	**C11**	6.26	2.13
C6	3.00	1.45	**C12**	7.20	3.29

*__A1–A18__ in dimethylformamide, **B1–B7** and **C1–C12** in ethanol.

RESULTS AND DISCUSSION (FIGURES 2 AND 3)

If V_i^{uv} and V_j^{fl} represent the wavenumbers in a solution having absorption corresponding to the energy change from S_{00} to S_{1i} and fluorescence corresponding to that from S_{10} to S_{0j}, respectively, it was assumed that the $(V_{\mathrm{max}}^{\mathrm{uv}} - V_0^{\mathrm{uv}})$ value was k times that of the low frequency half-value component H (eqn (2)).

$$H = (V_{\mathrm{max}}^{\mathrm{uv}} - V_0^{\mathrm{uv}})/k \quad (1 < k < \infty, 0 < i = \mathrm{max} < n) \tag{2}$$

A similar eqn (3) pertains for the high frequency half-value component H' on fluorescence,

$$H' = (V_{\mathrm{max}}^{\mathrm{fl}} - V_0^{\mathrm{fl}})/k' \quad (1 < k' < \infty, 0 < j = \mathrm{max} < m) \tag{3}$$

Combination of eqn (2) and (3) affords eqn (4)

$$\text{Stoke's shift } = V_{\mathrm{max}}^{\mathrm{uv}} - V_{\mathrm{max}}^{\mathrm{fl}} = kH + k'H' + V_0^{\mathrm{uv}} - V_0^{\mathrm{fl}} \tag{4}$$

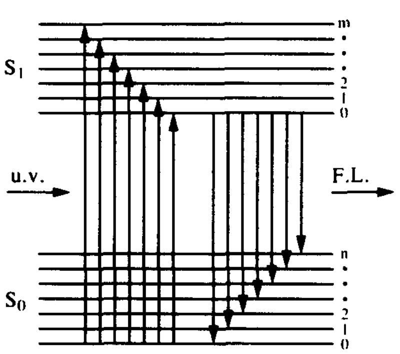


Fig. 2. Vibration energy level and electronic transition between states. S_0: ground state; S_{0j}: jth vibration energy level on S_0, $j=0, 1, 2, \ldots, n$. S_1: singlet excited state; S_{1i}: ith vibration energy level, $i=0, 1, 2, \ldots, m$.

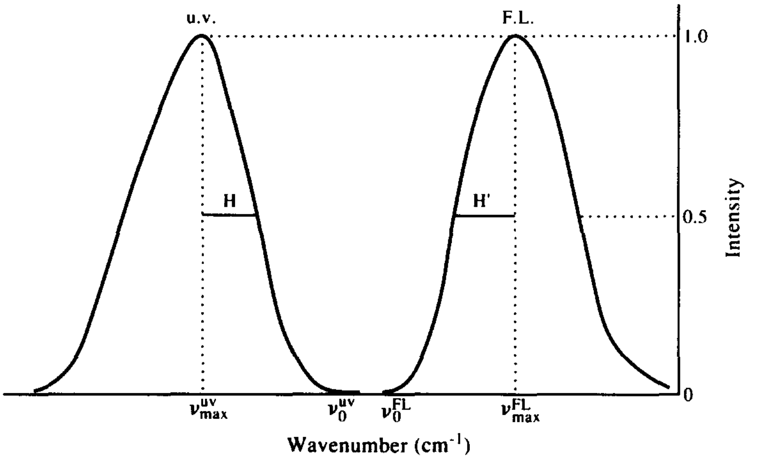


Fig. 3. Illustration of the relationship between absorption and fluorescence.

According to the 'mirror symmetrical rule' between fluorescence and absorption spectra, $k = k'$, $H = H'$, and if $b = V_0^{uv} - V_0^{fl}$, then the Stoke's shift is given by eqn (5).

$$\text{Stoke's shift } = 2kH + b \quad (1 < k < \infty) \tag{5}$$

The relationship between the Stoke's shift and the low frequency half-value component of naphthalimide type fluorescent dyes **A1–A18**, DNA intercalative dyes **B1–B7** and benzoxazole dyes **C1–C12** was studied and a good linear relationship between the Stoke's shift and H value was obtained, with linear correlation eqns (6), (7) and (8) respectively, as follows (see Fig. 4):

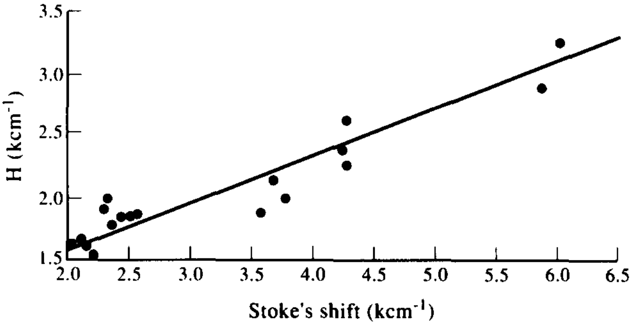


Fig. 4. Correlation between Stoke's shift and low frequency half-value component of compounds **A1–A18**.

$$\text{A : Stoke's shift} = 2.74H - 2.32 \quad (\text{k cm}^{-1}) \tag{6}$$

$$N = 18, r^2 = 0.889, s = 0.4453, F_{1,16} = 127.84$$

$$\text{B : Stoke's shift} = 2.66H - 0.239 \quad (\text{k cm}^{-1}) \tag{7}$$

$$N = 7, r^2 = 0.890, s = 0.8968, F_{1,5} = 40.28$$

$$\text{C : Stoke's shift} = 2.26H + 0.249 \quad (\text{k cm}^{-1}) \tag{8}$$

$$N = 12, r^2 = 0.822, s = 0.6450, F_{1,10} = 46.30$$

It was found that in a solution system, there was a linear correlation between the Stoke's shift and the low frequency half-value component for a series of fluorescent molecules, and it was also noted that whilst the coefficient for H was always greater than 2, it did not exactly equal the 2.5 value of the Pestemer's rule, and that the intercepts b in the above equations were usually constant, and not zero as shown in Pestemer's rule.

It was found that, when $b = 0$, the absorption spectrum intercepted with the fluorescence spectrum at the point of V_0^{uv} or V_0^{fl}; that when $b > 0$, the two spectra were separated, no overlap area existing between them, and that when $b < 0$, an overlap area was present between both spectra (spectral self-absorption). The correlation eqn (8) corresponds to the second case, and eqns (6) and (7) to the last case, i.e. consistent with the observed spectra.

In addition to being used for the experimental correlation of the Stoke's shift with the low frequency half-value component, or for their experimental prediction, eqn (5) could also be used as a basis for the theoretical calculation or prediction of the low frequency half-value component from the energy difference between the excited energy and the emission energy calculated theoretically. Using the PPP-SCF(β,γ)-CI method, we have obtained satisfactory calculation results for some dyes.[10]

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