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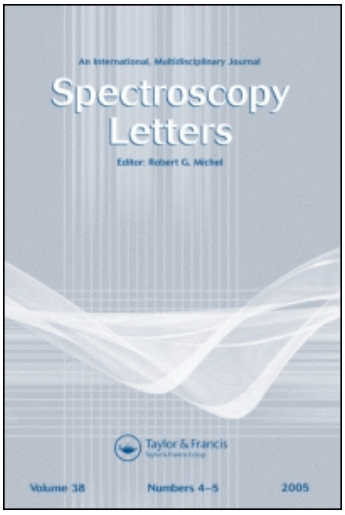

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Bernard Vidal[a]
[a] Université de La Réunion, Faculté des Sciences, La Réunion, FRANCE D.O.M.

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EFFECTS OF STRONGLY PERTURBATING AUXOCHROMES ON THE INTENSITY OF THE SECONDARY TRANSITION OF THE BENZENE CHOMOPHORE. THE PHENOLATE ANIONS.

Bernard VIDAL

Université de La Réunion, Faculté des Sciences, 15 avenue René Cassin, B.P. 7151, 97715 - Saint Denis messag. cedex 9 (La Réunion, FRANCE D.O.M.)

Abstract. The *Interaction Vector Model* (IVM) is used to study the intensity of the near UV transition of phenolates. Thirteen phenolates have been studied using the phenolate anion as a reference. The modulus of the $-O^- \Leftrightarrow -CH_3$ ortho interaction vector has been adapted to an unusual strong interaction. The π donating effect of $-O^-$ tends to blur the smaller π donating effect of the methyl substituents, and tends to quench the effect on intensity of the methyl in the para position.

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I - THE INTERACTION VECTOR MODEL

When the D_{6h} symmetry of the benzene molecule, which makes the secondary transition (255-260 nm) of that molecule forbidden, is destroyed by some substituents the intensity increases all the more as the perturbation increases. The intensity of the secondary transition of the benzene chromophore has been studied on the ground of the *Interaction Vector Model* [1-6] (IVM) for about one hundred molecules. Nevertheless, it has never been used to understand the changes of intensity when the chromophore bears a very strong perturbating substituent.

In this work our aim is to test whether the IVM still is valid when a substituent such as $-O^-$ (phenolate derivatives) is used. The problem met is the medium. Although there are many spectra in the literature, a few of them only is of interest since, very often, molecules are partly protonated. This superimposes the spectrum of the corresponding phenol molecules to the spectrum of the phenolates and blurs the structures, preventing to obtain the phenolate part with accuracy enough.

The $-O^-$ substituent displays a negative charge which makes it a very strong π donor substituent. The π system of the benzene moiety is strongly coupled to the oxygen p "non bonding" orbital of π symmetry. Intensity is very much increased compared to phenol (see underneath). The strong coupling between the benzene π system and the oxygen atom, increases the delocalization space for the π electrons. Thus, on the ground of the simple free electron model, one understands that the wave-

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length of the low energy transition (the secondary transition) increases, shifting towards the visible region (phenol λ_{max} = 270 nm ; medium : water ; phenolate : λ_{max} = 287 nm. medium : water + KOH, pH = 12.3).[7a,b]

Within the IVM [1,2] the SKLAR's [8] vector scheme is used with basis vectors **n** [1,2] (Figure 1) whose moduli n depend on the nature of the substituents. New concepts have been introduced : the *interaction vector* (Fig. 1a), which takes into account the interaction of two given substituents, the *strain vector* related to the strain imposed by fused rings when necessary. An interaction vector lies on the line bisecting the angle of the two basis vectors involved in the interaction (Fig. 1). It points in the same direction as the projection — on the bisectrix — of these basis vectors for ortho and meta interactions, in the opposite direction for the para interaction vector. The next values for the lengthes of the vectors are used :

basis vectors : $-CH_3 : n_c = 0.0980$; $-OR : n_o = 0.3900$

	$-CH_3 \Leftrightarrow -CH_3$	$-OR \Leftrightarrow -OR$	$-OR \Leftrightarrow -CH_3$
ortho interaction vector	0.0060	0.1330	0.0520
meta interaction vector	0.0060	0.0450	0.0240
para interaction vector	0.0120	0.1800	0.0630

A component related to a sort of *photonic cross section* is used too (see S and σ underneath). Its value increases as the substituents coupled to the π system enlarges this system increasing its efficiency to capture photons. A vibrational component [1,2,9] : V, takes into account the coupling of the vibrational motion to the electronic one. S and σ (σ = $S^{1/2}$) are functions of the number and of the nature of the substituents (n_C is the number of alkyl substituents, n_O the number of -OR ones) :

$$V = 0.0180 + 0.0390\,K + 0.0030\,(n_C + n_O) \quad ; \quad \text{if } n_O = 0 : K = 0 \text{ ; if } n_O \neq 0 : K = 1$$

$$S = [5n_O/(4{,}8 + 0.2\,n_O^2)] + n_C/(4{,}8 + 0.2\,n_C^{(2 + 0.5\,n_O)})$$

since : $S = hn_x/(4{,}8 + 0.2\,n_x^2)$, for a given substituent X. h is a constant depending on the nature of X. The vectors **S** and **n** diplay the same direction. a is : $a = n^{1.5}\sigma^{0.5}$, and b : $b = n(n + \sigma)/2$. Then : $p = (a + kb)/(1 + k)$, with $k = d^6$, and : $d = |n - \sigma|$.

Intensity is given as ε_{sm}, the maximum of the smoothed absorption curve (BALLESTER and RIERA [9]) (the calculated value is : $\varepsilon_{sm,c}$). This approach minimizes the incidence of the vibrational fine structure on the measure of intensity. A general relationship has been obtained [1,2] :

$$\varepsilon_{sm,c} = 4905\,[1.025\,p + V]$$

II - THE PHENOLATE TYPE ANIONS

a) The phenolate anion

It is impossible to use the relationships which have been determined in previous works [5] to calculate n, σ and V for the $-O^-$ substituent.

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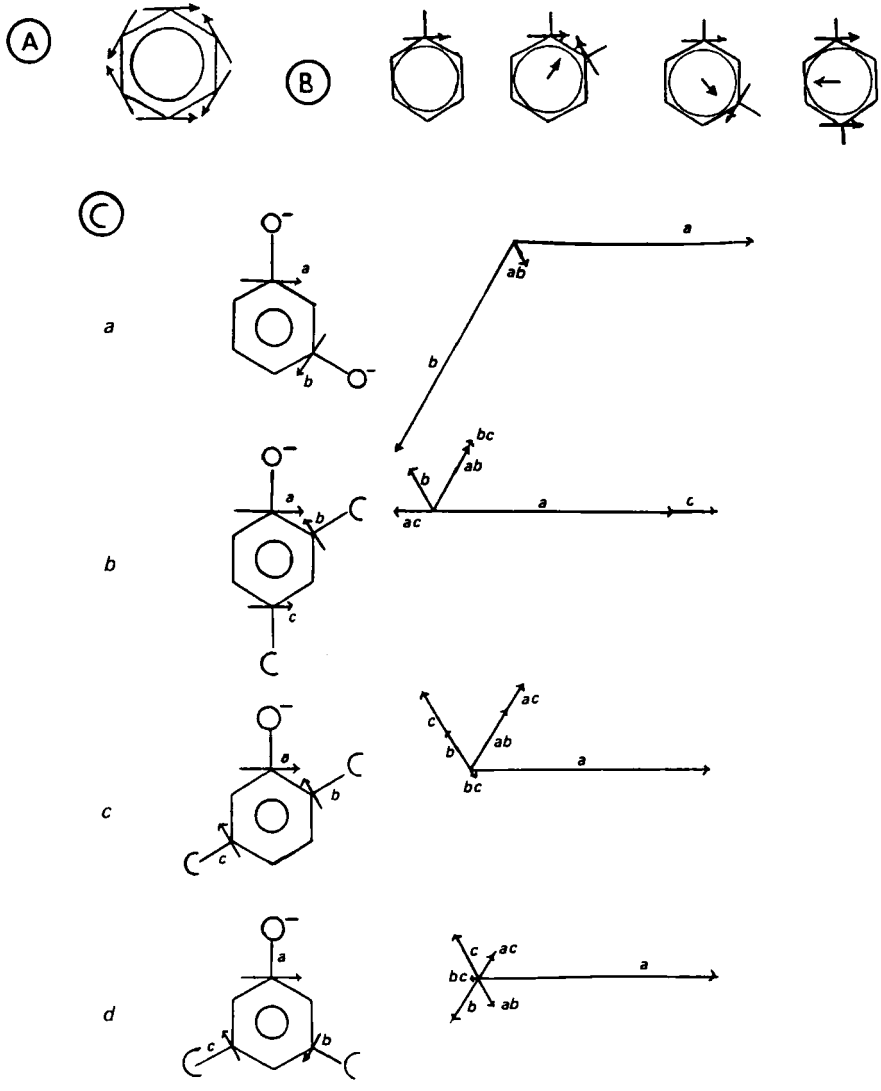

FIGURE 1. A) The Sklar's basis virtual vectors pattern. B) The basis vectors corresponding to the positions of the substituents. The interaction vectors have been drawn inside the benzene ring. All the directions are relative within a given molecule. C) Some examples of vector additions. a) $n_a = 0.495$, $n_b = 0.495$, $n_{ab} = 0.0571$. This gives : n = 0.5521. b) $n_a = 0.495$, $n_b = 0.098$, $n_c = 0.098$, $n_{ab} = 0.1487$, $n_{ac} = 0.0828$, $n_{bc} = 0.006$. This gives : n = 0.5813. c) $n_a = 0.495$, $n_b = 0.098$, $n_c = 0.098$, $n_{ab} = 0.1487$, $n_{ac} = 0.0657$, $n_{bc} = 0.012$. This gives : n = 0.6159. d) $n_a = 0.495$, $n_b = 0.098$, $n_c = 0.098$, $n_{ab} = 0.0657$, $n_{ac} = 0.0657$, $n_{bc} = 0.006$. This gives : n = 0.4567. In the drawings the letter C stands for $-CH_3$.

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Actually, the MNDO method which has to be used for such a determination is not perfectly able to deal accurately with charged species. It amplifies too much the distorsions of charges. So, one has choosen among the already studied molecules those which display almost the same intensity as the phenolate anion. This allows to interpolate and find the values of n, σ and V which can lead to the same molar extinction coefficient as the phenolate anion (ε_{sm} = 2400, medium : methanol + NaOH). That value is between :

ε_{sm} = 2550 ; n = 0.523 ; σ = 1.336 ; V = 0.063 (1,2-dihydroxybenzene)

and

ε_{sm} = 2000 ; n = 0.435 ; σ = 1.336 ; V = 0.063 (1,3-dihydroxybenzene)

This leads to n = 0.495, σ = 1.336, V = 0.063 for the phenolate anion. Of course other groups of values could be mathematically consistent to obtain the molar extinction coefficient of the phenolate anion. Nevertheless, the above ones correspond to a case consistent on a spectroscopic ground.

The value of σ leads to S = 1.7849, this fixes the parameter h in $S = h n_O^{-}/(4{,}8 + 0.2\, n_O^{-2})$: h = 8.9245. This allows to obtain : a = 0.4025, b = 0.4532, d^6 = 0.3538, thus : p = 0.4158, and as V = 0.063 :

$$\varepsilon_{sm,c} = 4905\,[1.025 \cdot 0.4158 + 0.063] = 2400$$

which is the value that has to be obtained.

Following the same policy as that used in previous works and explained above when defining V, one will add 0.003 to V, for each substituent added around the benzene ring.

One should mention that too many negative charges around the benzene ring, interacting strongly with the π system of the ring, could change the nature of the transition. For example, the 1,3,5 $-O^-$ trisubstituted benzene displays a very high intensity (ε = 8730) [11] when the positions of the substituents should lead for symmetry reasons to a very weak intensity. The same happens for the 1,2,3 trisubstituted ring (ε = 4600) [11]. In the first case, at least, one can hardly keep on with speaking of a symmetry perturbed transition : S and σ are very strong (for these two latter molecules : S = 4.057, σ = 2.014). One can assume that the photonic cross section approach should prevail over the symmetry one, since the chromophore being strongly changed there is no such thing as a secondary transition. The observed transition should no more obey to the restriction imposed by the D_{6h} symmetry, or a slightly distorted D_{6h} symmetry. IVM is applied to symmetry perturbations, not to complete loss of the D_{6h} symmetry imposed by too important migrations of charges. To study the two above molecules it should be necessary to produce new values for the IVM parameters adjusted to the powerful π donating effects of the three $-O^-$ substituents.

b) Resorcinol dianion (meta derivative)

Since it is a correction, the modulus of the interaction vector between two substituents is assumed [1-6] to be proportional to the modulus of the basis interacting vectors. One starts from the values, given here above, obtained for -OR substituents — since these values are

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the nearest possible to the $-O^-$ ones —, one multiplies by 0.495/0.390 = 1.269 (0.495 being the basis vector length for $-O^-$ as obtained above ; 0.390 being the basis vector length for -OR). Thus :

$-O^- \Leftrightarrow -O^-$ interaction in the : (ortho position: 0.1688)
meta position : 0.0571
para position : 0.2284

The value for the ortho position is inside brackets because the neighbouring of two negative charges could change the nature of the perturbation.

Litterature does not display many secondary transition intensities consistent enough to evaluate vectors moduli for $-O^-$ interactions (overlaps of transitions prevent to observe the scondary transition, or an unsufficient basic medium mixes the spectra of phenol and phenolate species). The only molecule found is the meta derivative. The vector addition is given in figure 1C-a. The interaction vector involving the two $-O^-$ substituents being 0.0571 long, the vector addition gives : n = 0.5521. S = 3.1873, thus σ = 1.7853. This leads to : a = 0.5481, b = 0.6452, d^6 = 3.5172, p = 0.6237, and :

$$\varepsilon_{sm,c} = 4905\ [1.025 \cdot 0.6237 + 0.066] = \mathbf{3460}, \text{ experiment : } 3400\ ^{10a}$$

The difference between calculation and experiment is Δ = + 1.75 % considering experiment as the reference. It has been estimated in previous works that a calculation leading to a value differing less than 10 % from the experiment is quite satisfactory.

c) Resorcinol anion (meta derivative)

Although one does not possess the values of many derivatives with two $-O^-$ substituents, some of them display one $-O^-$ and one -OH. The calculation of the interaction vector between $-O^- \Leftrightarrow$ -OH is done using the geometric average (g_1) and the arithmetic average (a_1) between the interaction vectors of $-O^- \Leftrightarrow -O^-$ and -OH $\Leftrightarrow$ -OH, as it has been shown in a preceding work [1]. Then, the geometric average and the arithmetic average of g_1 and a_1 are calculated giving g_2 and a_2 and the process is repeated using g_2 and a_2 until convergence towards the same value $g_i = a_i$ is reached. In the present case, starting from : 0.0571 and 0.0450 one obtains 0.0509 for the meta $-O^-$,-OH derivative. Thus : n = 0.5017, a = 0.4591, b = 0.5445, d^6 = 2.527, p = 0.5203, and :

$$\varepsilon_{sm,c} = 4905\ [1.025 \cdot 0.5203 + 0.066] = \mathbf{2940}, \text{ experiment : } 2700\ ^{10b};\ \Delta = +8.9\ \%$$

d) Pyrocatechol anion (ortho derivative)

The $-O^-$,-OH ortho derivative is known. The calculation of the ortho interaction vector is made as it has been done above for the meta $-O^-$,-OH one.

The modulus of the ortho interaction vector of $-O^- \Leftrightarrow -O^-$ is 0.1688, for -OH $\Leftrightarrow$ -OH it is : 0.1330. This gives : 0.1504 for the $-O^-$,-OH ortho one. Thus n = 0.6029, a = 0.6049, b = 0.6849, d^6 = 1.4660, p = 0.6517 :

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$\varepsilon_{sm,c} = 4905\ [1.025 \cdot 0.6049 + 0.066] = \mathbf{3600}$, experiment : 3500 [11], $\Delta = +2.9\ \%$

One could argue that it could exist a strong ortho interaction between the two neigbouring substituents : $-O^-$ and -OH. There is the possibility of an exchange of the hydroxy hydrogen between the two oxygens, or a sharing of the hydrogen by the two oxygens. This could change completely the nature of the problem. In fact, the exchange would not change the value obtained since the proton would be on one of the oxygen or on the other, and the two oxygens display the same surroundings. As concerns the sharing of the proton by the two oxygens, one would have two identical substituents with for each of them a basis vector being the average of the basis vectors for -OH and $-O^-$ and this would change only very slightly the value obtained here above.

e) Methyl substituted phenolate anions

The methylated phenolate ions ($-O^- \Leftrightarrow -CH_3$) can be used too to test the IVM. The modulus of the interaction vector is calculated as above. For the ortho derivative the methyl interaction vector being 0.0060, and for the $-O^- \Leftrightarrow -O^-$ derivative : 0.1688, the $-O^- \Leftrightarrow -CH_3$ interaction vector should be : **0.0561**. For the meta $-O^- \Leftrightarrow -CH_3$ derivative the value should be **0.0248**. For the para derivative : **0.0828**. Doing the same for the $-OH \Leftrightarrow -CH_3$ interactions, in a preceding work, the calculated values had been slightly improved on an empiric ground. This improvement had been possible because one had a lot of experiment data on methyl phenols. As concerns the phenolate group and the methyl one, the value of the basis vector length for the methyl substituent being very weak, it is known with a low accuracy and, consequently, the values of the lengthes of the interaction vectors are known with a low accuracy too.

Using the above values the calculation for the ortho derivative would give $\varepsilon_{sm,c} = 2525$, when experiment gives 3100 [12a]. This is strongly bad. This could be a specific behaviour for that molecule. In fact, for the three other molecules studied in this work which display such an ortho interaction the calculated value is far much too low (about : 10 to 25%). This is a strong and constant discrepancy. One has to assume the existence of a specific ortho interaction between $-O^-$ and $-CH_3$. Using as a reference the derivative with one methyl in the ortho position to an $-O^-$, one has to multiply by 2.65 the value obtained for the ortho interaction to obtain a satisfactory result : $0.0561 \cdot 2.65 = \mathbf{0.1487}$. This is an important change. This new value leads also to satisfactory results for the three other molecules displaying an ortho interaction.

One could think that if a strong interaction is observed with $-O^- \Leftrightarrow -CH_3$, it should be observed too in the $-O^-$,-OH ortho derivative (pyrocatechol anion). In fact, if an ortho interaction exist in the pyrocatechol anion its nature differ from that involved by $-O^- \Leftrightarrow -CH_3$, since the two oxygen sites can fix a proton. It has been seen here above that such an interaction would not perturb strongly the intensity.

The modulus of the ortho interaction vector is greater than the basis vector of one of the interacting substituents : $-CH_3$. This is the first time that such a phenomenon is observed. That means that when an $-O^-$ substituent is in a molecule it strongly changes the electronic effects imposed to the benzene chromophore by an ortho methyl. This arises

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because the length of an interaction vector depends on the lengthes of the two basis vectors. One of them being very long (the $-O^-$ one) the interaction vector is long, and it is increased by the specific ortho interaction (x2.65). No theoretical point opposes to the fact that an interaction vector can be longer than a basis vector.

Some vector addition schemes are given in figure 1.

- For the **2-methylphenol anion** (the $-O^-, -CH_3$ ortho derivative) : S = 1.9849 and σ = 1.4089, n = 0.5625 using the value 0.1487 for the interaction vector. As there are two substituents, one being an $-O^-$ one : V = 0.066. Thus $\varepsilon_{sm.c}$ = **2915**. Experiment gives : 3100 [12a] (Δ = - 6.0 %).

- For the **3-methylphenol anion** (the $-O^-, -CH_3$ meta derivative) : S = 1.9849 and σ = 1.4089. n = 0.4706, a = 0.3832, b = 0.4422, d^6 = 0.6824, p = 0.4071, $\varepsilon_{sm.c}$ = **2370**. Experiment gives : 2545 [12b] (Δ = - 6.8%).

This is satisfactory. Nevertheless, if one uses the same correction (x2.65) as above for the ortho derivative, the meta interaction vector is : 0.0248·2.65 = **0.0657**. This leads to : n = 0.4994, a = 0.4189, b = 0.4641, p = 0.4480, and : $\varepsilon_{sm.c}$ = **2575** (Δ = - 1.3%). The strong increase of the interaction vector modulus increases the calculated molar extinction coefficient from 2370 to 2575, that is to say 8.6 %. This increase is noteworthy but weak compared to the fact that the length of the interaction vector has been multiplied by 2.65. Actually, the meta interaction vector modulus is short. It contributes only weakly to intensity.

- As concerns the **4-methylphenol anion** (the para derivative), the methyl derivative is not available, but a $-CH_2-R$ substituent is $[-CH_2CH(CO_2CH_2CH_3)NHCOCH_3]$. It has been established in a preceding work, [2] that an ethyl like substituent displays a slightly shorter basis vector than the methyl substituent (the small changes concerning the interaction vectors have always been neglected). Its value is 0.090. Thus for this latter molecule : n = 0.5022, a = 0.4224, b = 0.4799, d^6 = 0.5556, p = 0.4429, $\varepsilon_{sm.c}$ = **2550**. Experiment gives : 2400 [10c] (Δ = + 6.3 %). One should notice that the interaction vector in the para position is almost as much important as the methyl basis vector. As the direction of the para interaction vector is opposed to the direction of the basis vectors, such a strong amplitude of the interaction vector means that the effect, on the intensity, of a methyl in the para position to a $-O^-$ substituent is almost zero. The $-O^-$ substituent quenches almost all the effect of the para methyl group on intensity. There is no need to change the value of the interaction vector in the para position, although it would decrease the calculated value, improving that value.

- Considering the **2,3-dimethylphenol anion** using the ortho and meta interaction vectors increased by the factor 2.65 (0,1487 and 0.0657) one obtains : n = 0.5034. σ = 1.4567, a = 0.4311, b = 0.4934, d^6 = 0.7505, p = 0.4578, and as V = 0.069 : $\varepsilon_{sm.c}$ = **2640.** Experiment gives : 2900 [10d] (Δ = - 9.0%). This is not perfect but within the margin of error.

- As concerns the **2,4-dimethylphenol anion** — which displays a para interaction vector — using for the ortho interaction vector the corrected value (x2.65 ; i.e.: 0.1487) : n = 0.5813, a = 0.5349, b = 0.5923, d^6 = 0.4500, p = 0.5527, $\varepsilon_{sm.c}$ = **3117**. Experiment : 3000 [12d] (Δ = + 3.9 %).

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- The **3,4-dimethylphenol anion** does not display the strong ortho interaction. Using the corrected value for the interaction, calculations lead to : n = 0.5183, σ = 1.4567, a = 0.4504, b = 0.5145, d^6 = 0.6829, p = 0.54764, $\varepsilon_{sm.c}$ = **2735**. Experiment gives 2785 [12e] (Δ = - 1.9 %).

- The **2,5-dimethylphenol anion** displays the ortho interaction and the meta one : n = 0.6159, σ = 1.4567, a = 0.5834, b = 0.6383, d^6 = 0.3533, p = 0.5947 and : $\varepsilon_{sm.c}$ = **3345**. Experiment gives 3450 [12f] (Δ = - 3.1 %).

- The **3,5-dimethylphenol anion** displays only meta interactions : n = 0.4567, σ = 1.4567, a = 0.3725, b = 0.4369, d^6 = 1, p = 0.4047 and : $\varepsilon_{sm.c}$ = **2375**. Experiment gives 2605 [12g] (Δ = - 8.8 %)

CONCLUSION

The *Interaction Vector Model*, used to calculate the intensity of the secondary transition of the benzene chromophore, is able to deal with the strong π donating effect of one $-O^-$ substituent (phenolates) and of its methyl derivatives. The model cannot lead to good results when there are three $-O^-$ substituents. It has not been designed for such strong charge transfer from the substituents to the chromophore. These strong effects change completely the nature of the transition, and change the fact that the intensity of the transition depends on the symmetry D_{6h} of the π system of the chromophore. The photonic cross section approach could prevail.

The π donating effect of the $-O^-$ substituent tends to blur the smaller π donating effect of the methyl substituents, and tends to quench the effect on intensity of the methyl in the para position. This is the case too for the whole studied molecules, whose observed and calculated intensity values lie inside a narrow field. A strong ortho interaction ($-O^- \Leftrightarrow -CH_3$), whose origin has not been discussed, imposes to adapt the modulus of the interaction vector.

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