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A Spectroscopic Rule from the Solvatochromism of Aromatic Solutes in Nonpolar Solvents

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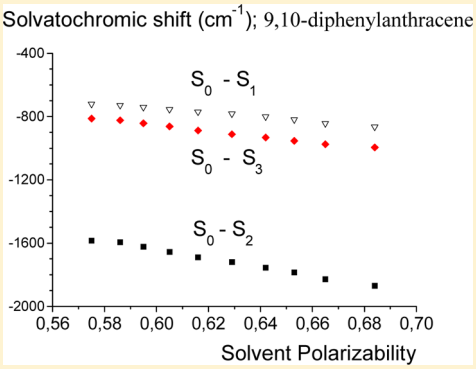
ABSTRACT: The UV−vis absorption spectroscopy for a series of selected symmetrical aromatic hydrocarbons, benzene, naphthalene, anthracene, 9,10-diphenylanthracene, perylene, and rubrene in the gas phase or in 2-methylbutane, shows the consistency of a new spectroscopic rule. From a thorough spectroscopic analysis with temperature variation (293−113 K) this rule states that "an aromatic molecule, on Franck−Condon excitation can hardly generate an excited electronic state with a lower polarizability than that of its ground electronic-state." We have not found any exceptions to this rule.



INTRODUCTION

The relationship between the effects of a solvent on an electronic transition of a given solute and the solvent properties was investigated by Kundt[1] in 1878 and led him to propose the following rule: "the increase of the dispersion effect of the solvent (cf. its index of refraction) is related to a shift of the absorption maximum of the solute toward a longer wavelength." It is known[2] that the UV−vis absorption spectra of a chromophore can be influenced by the phase state (gas, liquid, or solid matrices) and the properties of the solvent, and thus causing the electronic transitions of a solute to change not only in energy but also in intensity. The spectra can also be influenced by perturbing the envelope of the absorption band, thereby generating significant absorption changes compared to the gas phase. This phenomenon was named solvatochromism by Hantzsch.[3]

In 1950 Bayliss[4] concluded, by regarding the solvent as a continuous dielectric medium and by using arguments from the quantum theory and the classical dispersion theory, that the shift of the absorption to lower frequencies for a nonpolar solute in a nonpolar solvent is due to the solvation energy of the transition dipole. He indicated that the red shift depended on the intensity of the transition (measured by the oscillator strength of the transition), the solvent refractive index (n, as a function n^2), and the size of the solute molecule (such as the volume of the cavity a^3, a being the mean molecular radius). In 1953, Bayliss and Hulme[5] investigated this spectral behavior by studying the absorption spectra of benzene, toluene, and chlorobenzene in a set of media (i.e., gas, water, ethanol, n-hexane, cyclohexane, chloroform, and carbon tetrachloride).

Important contributions to the treatment of the solvent effect were made by Ooshika,[6] who disregarded the effect of the transition moment on the red shift, and by McRae[7] (eq 1) and Longuet-Higgins and Pople[8] who stated the contrary. The latter authors[8] (eq 2) concluded in their work that "the second term (M^2, *the squared transition dipole moment*) predicts an increased (*red*) shift for those transitions which are strongly allowed".

McRae−Bayliss equation

$$\bar{\nu}_{eg}^{sol} = \bar{\nu}_{eg}^{0} - \left[(\mu_g \cdot \mu_e \cos\varphi - \mu_g^2)\frac{1}{a_w^3}\right][L(\varepsilon_r) - L(n^2)] - \left[(\mu_e^2 - \mu_g^2)\frac{1}{a_w^3}\right][L(n^2)] \quad (1)$$

Equation 1 exemplifies the model developed by McRae and Bayliss, where $\bar{\nu}_{eg}^{sol}$ and $\bar{\nu}_{eg}^{0}$ are the solute transition energies in solution and in gas phase, respectively, φ is the angle between both permanent dipole moments $\mu_g \cdot \mu_e$, a_w^3 is the solute cavity radius, and $L(x) = 2(x - 1)/(2x + 1)$ with $x = n^2$ or ε_r.[22]

Longuet-Higgins and Pople equation

$$\text{red shift} = \frac{1}{6}\alpha_B z \bar{R}^{-6}\left[\frac{1}{4}E\alpha_A + M^2\right] \quad (2)$$

On the other hand, eq 2 exemplifies the model raised by Longuet-Higgins and Pople, where "red shift" is the solvatochromic shift, α_A and α_B are the molecular polarizabilities of the solute and solvent, respectively, M and E are the dipole moment and energy of the transition, and each solute molecule is supposed to be surrounded by z solvent molecules at a mean distance R.

Bakhshiev's[9] and Liptay's[10] contributions involved more rigorous approaches but retained the shift dependence on the

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transition moment that was introduced by Bayliss.[4] Liptay's approach implements three important approximations: (1) the solvent is approximated as a homogeneous and isotropic dielectric, (2) the solute molecule is placed in a spherical cavity, and (3) a point dipole moment is substituted for the dipole moment of the solute.

In 2008, Renger[11] et al. (eq 3, 4) defended to have theoretically demonstrated that a nonpolar solute in nonpolar media must accord with the following: (1) the higher is the energy of an excited electronic state the greater is its solvatochromic shift to the red for the corresponding absorption transition, eq 5 of their work (if $E_n > E_m$, then it holds that $\kappa_{n0} > \kappa_{m0}$), and (2) the red shift does not depend on the oscillator strength of the transition. These two points allowed Renger et al. to report a new spectroscopic rule that states "the larger the energy E_n of the excited state (of the solute), the larger the solvatochromic red shift", and to eliminate the contribution by Bayliss et al. regarding the shift-dependence on the oscillator strength of the electronic transition.

Renger, Grundkötter, Madjet, Müh equation

$$\Delta E_{n0} = \kappa_{n0}\frac{W_u}{d_u^2} \tag{3}$$

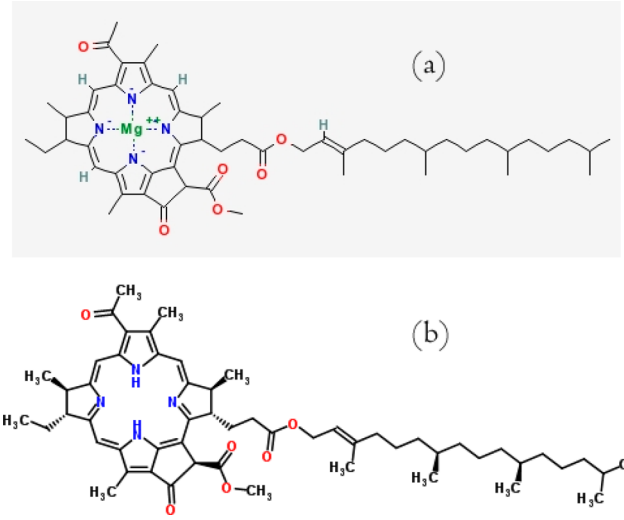
$$\kappa_{n0} = \sum_{k}^{k\neq n,0} (d_{nk}^2 - d_{0k}^2) \tag{4}$$

The solvatochromic shift ΔE_{n0} depends on the solvation energy W_u of an extended unit dipole (d_u= 1D). κ_{n0} depends on the transition dipole moments for the electronic transitions other than the relevant electronic transition under study—d_{n0}. Assuming a point charge dipole and a spherical cavity, the solvation energy W_u of eq 3 leads to $[-1/R^3\cdot(n^2 - 1)/(2n^2 + 1)]$,[11] the second term of eq 1 by Bayliss and McRae. But the squared permanent dipole moment difference of the solute in the ground (g) and excited (e) states ($\mu_e^2 - \mu_g^2$), which is a measure of the oscillator strength for the electronic transition under study, is substituted by κ_{n0}, which does not depend on the (transition) dipole moment of the electronic transition under study (d_{n0} or d_{eg}), and therefore κ_{n0} does not depend on the oscillator strength of the transition.

Renger et al. emphasized their model because of two reasons: (1) they made use of the oscillator strength sum rule and (2) they used an extended dipole instead of a point dipole. They successfully tested their theory of solvatochromism on the two lowest electronic excitations of *bacteriochlorophyll a* and *bacteriopheophytin a*; however, this success seems fortuitous owing to the great complexity of these molecular structures (Scheme 1). They exhibit scarce rigidity and C_1 symmetry, and their permanent dipole moment(s) may change significantly upon photoexcitation. The molecule *bacteriopheophytin a* is essentially a chlorophyll molecule with two hydrogen atoms replacing the magnesium center.

In any case, the polarizability of the excited electronic state of the nonpolar solute is greater than that of its ground electronic state epitomized red shift produced by a nonpolar solvent. However, the formulation of Renger[11] et al. is hard to accept spectroscopically because it indicates that the polarizability of a given excited electronic state increases as its energy also increases compared to the polarizability of the ground electronic state and also that this solvatochromic red shift is

Scheme 1. Molecular Structures for (a) *Bacteriochlorophyll a* and (b) *Bacteriopheophytin a*



not affected by the intrinsic intensity (oscillator strength) of a given electronic transition.

From the spectroscopic point of view it is accepted that upon excitation of one electron of the molecule, for instance, from an n or π molecular orbital in the ground electronic state to a π^* molecular orbital of the excited electronic state, the excited state molecular polarizability will significantly increase with respect to that in the ground electronic state. For the ground electronic state, the electron in a π molecular orbital is labile; the electron is more or less localized but is involved in chemical bonding and the electron in an n orbital is much more localized and forms a lone pair. Upon electronic excitation into a π^* molecular orbital, the electron gets more delocalized compared to the ground electronic state, and as a result, the excited state polarizability will be greater than that at the ground state. This behavior is consistent with the solvatochromism of acetone and its derivatives[12] which, as a matter of fact, can be streamlined based on that for these molecules. The polarizability of the electronic states involved in the various electronic transitions is greater than the ground-state polarizability.

In this work the inconsistencies of the sound spectroscopic rule proposed by Renger[11] et al. are unveiled, and another rule using UV−vis absorption spectroscopy at various temperatures is stated. The solvatochromism was analyzed for a series of nonpolar solutes (Scheme 2) that possess a rigid molecular geometry in the ground electronic state and sufficiently high symmetry to neglect the influence of their permanent dipole moments when increasing the excitation energy of the electronic transition. The selected solutes exhibited absorption bands that did not maintain a parallel increase of the intrinsic intensity (oscillator strength) of the transition as the transition energy increased. To this end, the following series of molecules was chosen: benzene, naphthalene, anthracene, 9,10-diphenylanthracene (DPA), rubrene, and perylene (Scheme 2).

The most significant spectral data of these compounds are gathered in Table 1 (all of them were extracted from Table 3.1 of the classic book by Birks[13]). The state numbering in Table 1 is merely used to indicate the energy order of the transitions for the sake of studying the solvatochromism in 2-methylbutane (2MB). The solvent polarizability of 2MB is changed by

Scheme 2. Aromatic Molecules of This Study

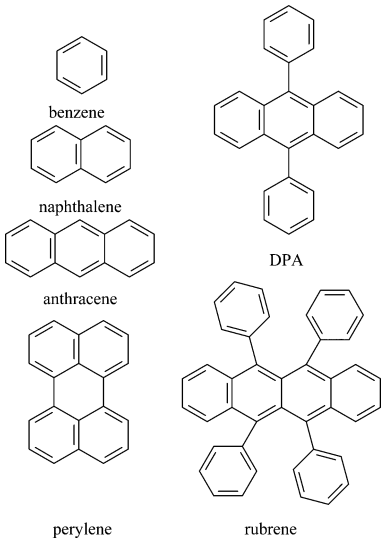


Table 1. Absorption Spectra $S_0 \rightarrow S_n$ for the Aromatic Molecules

compound	solvent	state	0−0	peak	ε_{max}[a]
benzene	hexane	S_1	38 400	39 300	250
		S_2		49 000	8800
naphthalene	hexane	S_1	32 200	33 200	270
		S_2	35 000	36 400	5600
		S_3	45 300	45 300	117 000
anthracene	hexane	S_1	26 700	26 700	8500
		S_2		not observed	
		S_3	39 700	39 700	220 000
		S_4		45 200	11 400
DPA	ethanol	S_1	25 500	26 800	12 600
		S_2		not observed	
		S_3	38 700	38 700	104 000
		S_4	44 300	44 300	22 000
perylene		S_1	23 000	23 000	39 500
		S_2		34 300	1400
		S_3		38 000	10 600
		S_4		39 600	53 000
rubrene	toluene (295 K)	S_1	20 202	20 202	26 000

[a]The transition energies in cm^{-1} are relative to the ground state, S_0.

adjusting the temperature between its boiling point, 303 K, and its melting point, 113 K.

■ EXPERIMENTAL SECTION

All of the solvents used were of the highest purity available. The solvents 2MB, hexane, and heptane were Merck Uvasol grade. The decalin was from Aldrich (purity, ≥99.98%; bp, 193 °C); the benzene was Merck Uvasol grade; the naphthalene was the Aldrich scintillation grade (purity, ≥99%), the anthracene was Aldrich ReagentPlus (purity ≈ 99%); the DPA was from Aldrich and was purified twice (purity, ≤99%); the rubrene was also from Aldrich (purity, ≥98%); and the perylene was from Aldrich Gold Mark (purity, ≥99%).

All UV−vis spectra were recorded on a Cary-5 spectrophotometer at variable temperatures from 113 to 293 K, using Suprasil quartz cells of 1 cm path-length that were fixed to the cryostat. Solution temperatures over the range 113−293 K were controlled by an Oxford DN1704 cryostat which was purged with dried nitrogen of 99.99% purity and equipped with an ITC4 controller interfaced to the spectrometers. The absorption spectra in the gas phase for benzene were recorded at 298 K and for naphthalene at temperatures ranging from 293 to 343 K. The temperature was controlled with a precision of ±0.1 °C with the aid of a Fisons−Haake D8 GH thermostat.

■ RESULTS AND DISCUSSION

The solvatochromism was evaluated by recording the UV−vis spectra for benzene, naphthalene, anthracene, DPA, rubrene, and perylene in 2MB between 113 and 293 K, using the corresponding gas phase spectra at 298 K as the offset (the absence of solvent) with exception of perylene, for which its absorption spectrum in a neon matrix at 4 K was employed as the offset.

Thereafter, the rule stated by Renger[11] et al. will be put to the test by comparing it with the experimental evidence mentioned above. This new evidence allows us to shed light on this topic and to enunciate another rule on solvatochromism.

Absorption Spectra for Benzene. Figure 1 shows the UV absorption spectrum of benzene in the gas phase. The presence of two bands is clear. One band is in the 230−260 nm region with onset at about 266.5 nm and having a first peak at 259.3 nm, 38567 cm^{-1}, (assigned to the component 0−1), which is taken as a reference for characterizing the absence of solvent and to evaluate the solvatochromism of the electronic transition $S_0 \rightarrow S_1$. Another absorption band starts at 215 nm, remaining intense at 190 nm, which exhibits a first peak at 200 nm, 50001 cm^{-1} (also possibly its component 0−1) that is also taken as a reference to estimate the solvatochromism of the electronic transition $S_0 \rightarrow S_2$.

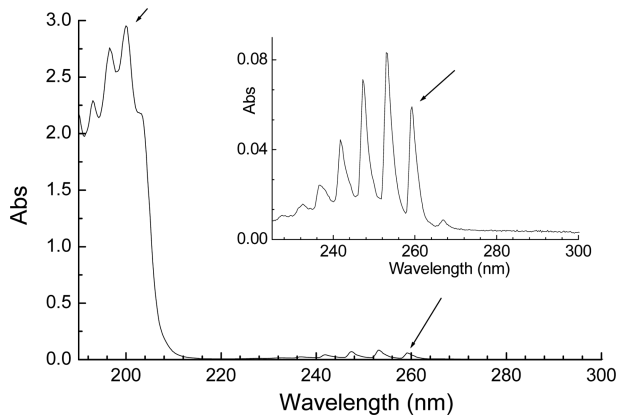


Figure 1. UV absorption spectrum of benzene in the gas phase. The arrows indicate the peaks regarded as standards for studying the solvatochromism of the corresponding electronic transitions when changing the solvent polarizability.

The solvent polarizability (SP, cf. the solvent polarizability scale) of 2MB increases as the temperature decreases from 293 K (SP = 0.575)[14] to 113 K (SP = 0.684) by keeping the solvent acidity (SA),[15] solvent basicity (SB),[16] and solvent dipolarity (SdP)[17] all at zero values. A small change in the polarizability of the medium of 0.11 units in the SP scale is enough to determine whether or not an electronic transition is sensitive to the polarizability of the medium.

Figure 2a shows the first absorption band of benzene in 2MB; that is, its transition $S_0 \rightarrow S_1$ at temperatures between 293 and 113 K is shown; Figure 2b shows the electronic

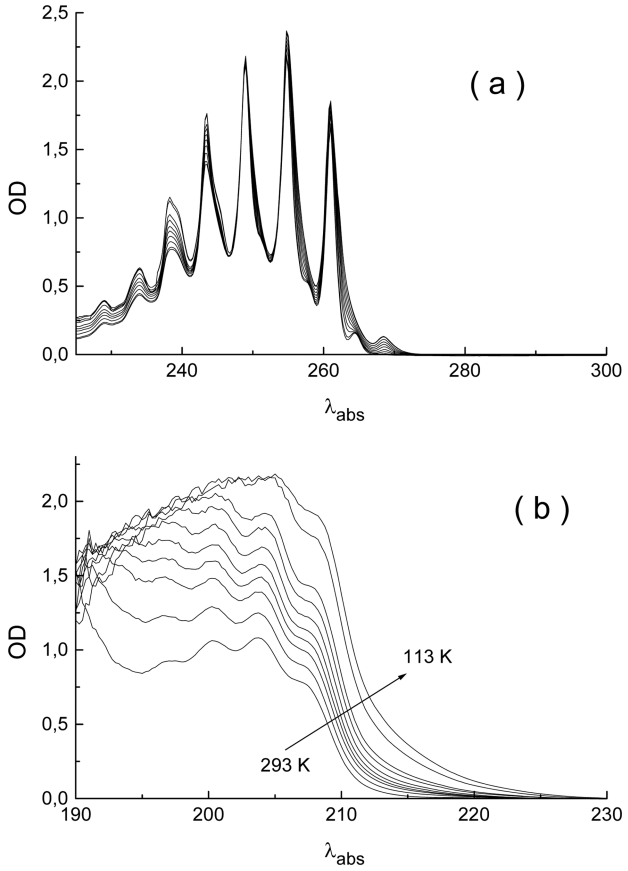


Figure 2. Absorption (absorbance, OD) spectra of benzene in 2MB recorded from 113 to 293 K. Absorption spectra for the electronic transitions (a) $S_0 \rightarrow S_1$ and (b) $S_0 \rightarrow S_2$ with temperature.

transition $S_0 \rightarrow S_2$ at the same temperatures. It is clear that while the $S_0 \rightarrow S_1$ transition is not sensitive to the solvent polarizability, the $S_0 \rightarrow S_2$ transition shifts to the red as the temperature decreases, that is, as the solvent-polarizability increases. Table 2 gathers the corresponding solvatochromic-shift values for both transitions, and it is clear that the $S_0 \rightarrow S_1$ transition yields a small red shift of about −250 cm^{-1} which is kept fairly constant with temperature, while the $S_0 \rightarrow S_2$ transition exhibits a greater red shift of about −908 cm^{-1} at 293 K which significantly increases to −1211 cm^{-1} at 113 K. The solvatochromism of benzene against the solvent polarizability value is shown in Figure 3.

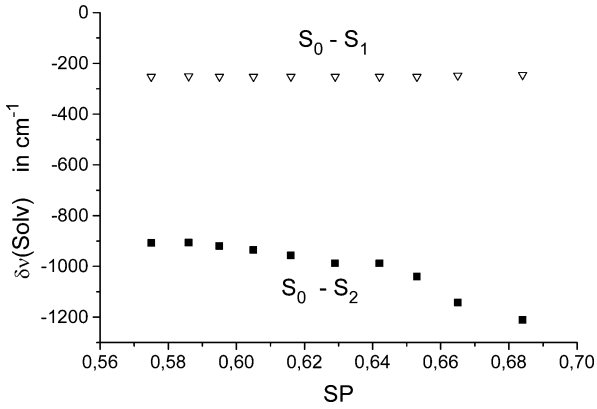


Figure 3. Solvatochromic shift for the electronic transitions of benzene $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ in 2MB against the solvent polarizability.

Absorption Spectra for Naphthalene. Naphthalene in the gas phase exhibits three electronic transitions in the UV region (Figure 4). The first band has an onset around 312 nm

Table 2. Electronic Transitions for the Aromatic Molecules in 2MB at Different Temperatures.

T (K)		293	273	253	233	213	193	173	153	133	113
gas phase[a]		2MB									
Benzene											
$S_0 \rightarrow S_1$	38 567	38 314	38 316	38 315	38 314	38 315	38 315	38 315	38 314	38 319	38 321
$S_0 \rightarrow S_2$	50 001	49 093	49 095	49 081	49 066	49 044	49 013	49 013	48 960	48 858	48 790
Naphthalene											
$S_0 \rightarrow S_1$	33 333	33 118	33 125	33 126	33 128	33 131	33 135	33 136	33 139	33 138	33 123
$S_0 \rightarrow S_2$	35 971	35 120	35 102	35 076	35 048	35 022	34 995	34 971	34 938	34 902	34 862
$S_0 \rightarrow S_3$	47 619	45 541	45 517	45 501	45 477	45 445	45 414	45 387	45 326	45 281	45 232
Anthracene											
$S_0 \rightarrow S_1$	27 457	26 732	26 715	26 700	26 685	26 666	26 646	26 625	26 606	26 587	26 570
$S_0 \rightarrow S_2$	42 270	39 806	39 781	39 746	39 701	39 654	39 611	39 572	39 532	39 479	39 429
DPA											
$S_0 \rightarrow S_1$	26 287	25 566	25 558	25 546	25 533	25 516	25 504	25 487	25 468	25 443	25 421
$S_0 \rightarrow S_2$	40 343	38 758	38 748	38 718	38 686	38 652	38 622	38 587	38 557	38 514	38 475
$S_0 \rightarrow S_3$	45 129	44 316	44 305	44 287	44 266	44 241	44 217	44 196	44 175	44 154	44 133
Rubrene											
$S_0 \rightarrow S_1$	19 735	19 144	19 145	19 115	19 094	19 067	19 037	19 015	18 987	18 951	18 909
$S_0 \rightarrow S_2$	34 740	33 532	33 510	33 485	33 438	33 399	33 375	33 322	33 285	33 228	33 170
$S_0 \rightarrow S_3$	44 828	44 595	44 594	44 631	44 618	44 617					
Perylene											
$S_0 \rightarrow S_1$	24 059	23 063	23 053	23 029	23 005	22 979	22 956	22 930			
$S_0 \rightarrow S_2$	34 977	34 365	34 364	34 314	34 317	34 297	34 277	34 269			
$S_0 \rightarrow S_3$	38 491	38 089	38 094	38 072	38 027	38 023	37 988	37 983			
$S_0 \rightarrow S_4$	41 152	39 730	39 726	39 716	39 706	39 696	39 681	39 668			

[a]The standard gas-phase electronic transitions at 298 K are implemented in the first column.

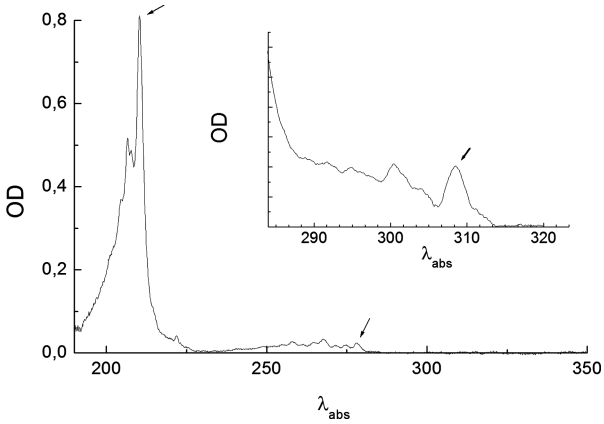


Figure 4. Absorption (OD, absorbance) spectrum of naphthalene in the gas phase. The arrows indicate the absorption peaks taken as solvatochromic standards.

and extends to 295 nm, which possesses an absorption peak at 300 nm (33333 cm^{-1}), possibly the 0−1 component of this electronic transition, and is taken as a reference to evaluate the solvatochromism. In addition, a second electronic transition was monitored with the onset around 288 nm and extending to 240 nm, and the third electronic transition has an onset at about 228 nm and extends to 190 nm. The intense peaks of these bands at 278 and 210 nm (35971 and 47619 cm^{-1}, possibly the 0−2 and 0−3 components, respectively) are taken as references, respectively, for offsetting the solvatochromism.

Table 2 collects the corresponding solvatochromic shifts for all of the transitions of naphthalene in 2MB, and it is clear that the $S_0 \rightarrow S_1$ red shift corresponds to a small value of about −160 cm^{-1} which is constant; the $S_0 \rightarrow S_2$ yields a lower value of −832 cm^{-1} at 293 K which significantly decreases down to −1090 cm^{-1} at 113 K. The third electronic transition is much more sensitive to the medium polarizability having a value of −1966 cm^{-1} at 293 K and reaching −2275 cm^{-1} at 113 K. Figure 5 shows the naphthalene solvatochromism against the polarizability of the medium.

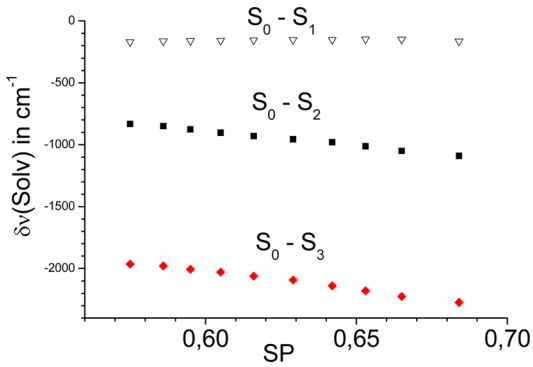


Figure 5. Solvatochromic shifts for the transitions $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$, and $S_0 \rightarrow S_3$ of naphthalene in 2MB against the medium polarizability.

Absorption Spectra for Anthracene and 9,10-Diphenylanthracene. The vapor absorption spectrum for anthracene was reported between 26 000 and 46 000 cm^{-1} by Ferguson[18] et al., and between 36 000 and 66 000 cm^{-1} by Lyons and Morris.[19] These authors placed the 0−0 component of the first electronic transition at 27 457 cm^{-1} and that of the second electronic transition at 42 270 cm^{-1}. Lyons and Morris[19] stated that in the spectral area of greater energy these electronic transitions involve a quasi-continuous Rydberg-type transition, and they also place the ^1C_b transition near 46 000 cm^{-1}.

Figure 6 shows the absorption spectra of anthracene obtained in 2MB with temperatures between 293 and 113 K.

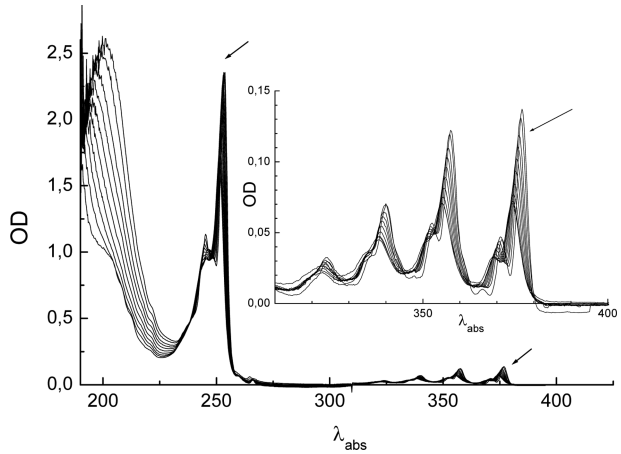


Figure 6. UV absorption spectrum for anthracene in 2MB recorded from 293 to 113 K. The arrows point to the absorption peaks taken as references of the respective electronic transitions.

The absorption peaks used for reference have been marked with an arrow in order to estimate the solvatochromism with respect to the gas phase. The solvatochromic data values are also gathered in Table 2. Figure 7 plots the solvatochromic shifts of the first two electronic transitions of anthracene in 2MB compared with the gas phase.

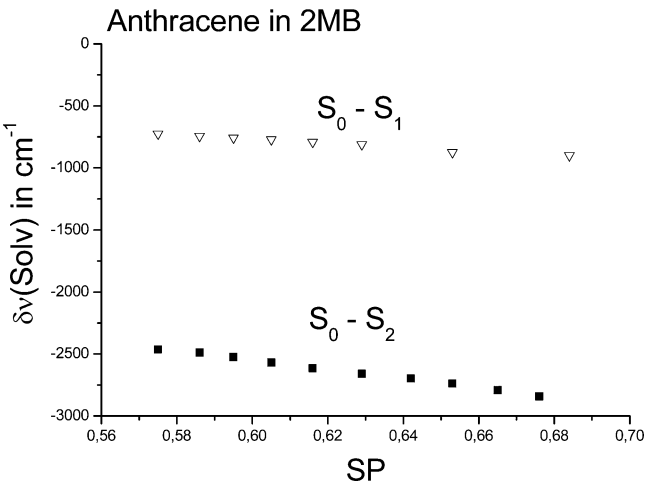


Figure 7. Solvatochromic shifts of both electronic transitions $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ for anthracene in 2MB against the medium polarizability.

Figure 6 shows some small spectral waving in the absorption envelope around 220 nm, which is possibly due to components of the ^1C_b electronic transition of anthracene, but they are not clear enough to be located and measured in 2MB; and therefore, the corresponding solvatochromism was not estimated. However, it is known that this composite electronic transition is more easily detectable in some substituted anthracenes such as DPA.

Figure 8 shows the spectra of DPA obtained in 2MB between 293 and 113 K. The arrows point to the components taken as

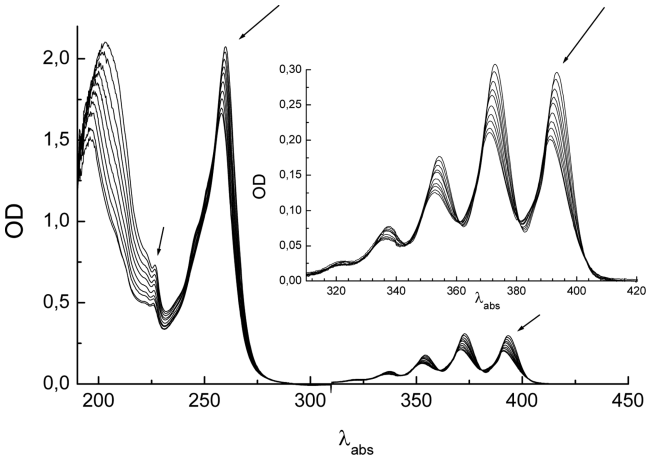


Figure 8. UV absorption spectrum (OD, absorbance) of DPA in 2MB recorded from 293 to 113 K. The peak maxima of the electronic transitions (indicated with arrows) are used for obtaining the solvatochromic shifts.

references to measure the solvatochromic shifts of the electronic transitions. The gas phase values have been estimated (for SP = 0) from the fits of the reference energy maxima of DPA in a set of *n*-alkanes:

$S_0 \rightarrow S_1$

$$\nu = -(1244 \pm 49)\mathrm{SP} + (26287 \pm 32) \quad (5)$$

with $n = 7$ data values, $r = 0.996$, and a standard deviation (SD) = 4 cm^{-1};

$S_0 \rightarrow S_2$

$$\nu = -(2697 \pm 90)\mathrm{SP} + (40343 \pm 59) \quad (6)$$

with $n = 8$, $r = 0.998$, and SD = 8 cm^{-1};

$S_0 \rightarrow S_3$

$$\nu = -(1483 \pm 111)\mathrm{SP} + 45129 \pm 72 \quad (7)$$

with $n = 6$, $r = 0.989$, and SD = 10 cm^{-1}.

Consequently, the gas phase components of the first three transitions for DPA are 26 273, 40 343, and 45 129 cm^{-1}. With the aid of these data and the corresponding spectral values in 2MB, which are shown in Figure 8, the solvatocromic shifts were calculated and implemented in Table 2 and are plotted in Figure 9 against the solvent polarizability.

Absorption Spectra for Rubrene. Figure 10 shows the spectra of rubrene obtained in 2MB between 293 and 113 K; the arrows point to the components taken as references to assess the solvatochromism. As for DPA, the gas phase values have been estimated (for SP = 0) from the fits of the peak energy maxima of rubrene in a set of *n*-alkanes

$S_0 \rightarrow S_1$

$$\nu = -(906 \pm 107)\mathrm{SP} + (19735 \pm 69) \quad (8)$$

with $n = 5$, $r = 0.980$, and SD = 9 cm^{-1};

$S_0 \rightarrow S_2$

$$\nu = -(2009 \pm 146)\mathrm{SP} + (34740 \pm 95) \quad (9)$$

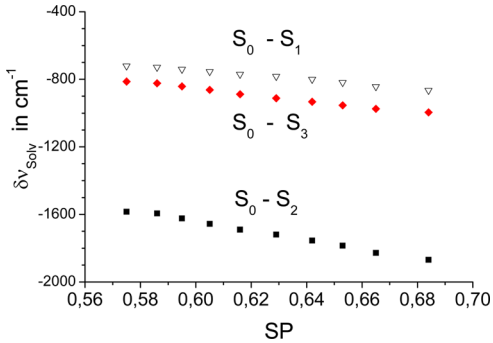


Figure 9. Solvatochromic shift for the electronic transitions $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$, and $S_0 \rightarrow S_3$ of DPA in 2MB against the solvent polarizability.

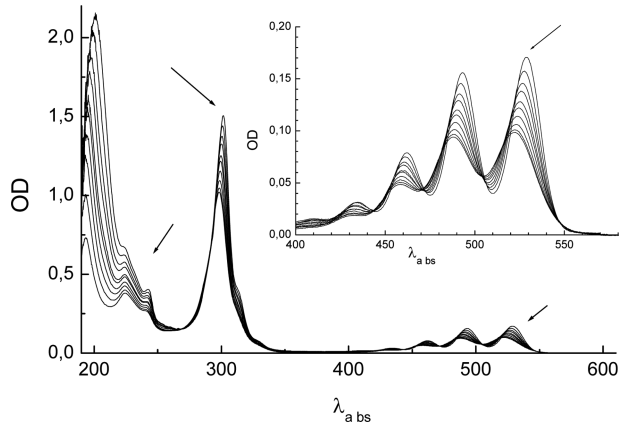


Figure 10. Absorption spectrum of rubrene in 2MB at temperatures between 293 and 113 K. The arrows indicate the peak maxima used as references to calculate the solvatochromic shifts in Figure 11.

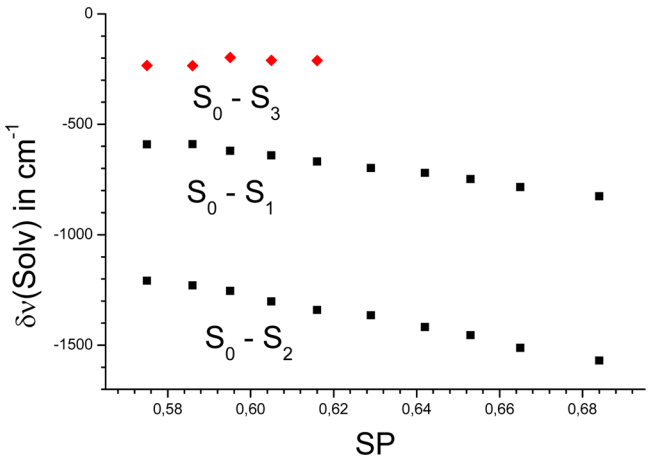


Figure 11. Solvatochromic shifts for the electronic transitions $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$, and $S_0 \rightarrow S_3$ of rubrene in 2MB against the solvent polarizability.

with $n = 5$, $r = 0.992$, and SD = 12 cm^{-1};

$S_0 \rightarrow S_3$

$$\nu = -(572 \pm 150)\mathrm{SP} + (44828 \pm 95) \quad (10)$$

with $n = 4$, $r = 0.938$, and SD = 11 cm^{-1}.

Consequently, the gas phase components of the three rubrene electronic transitions are 19 735, 34 740, and 44 828 cm^{-1}, extracted from eqs 8, 9, and10, respectively. The

corresponding solvatochromic shifts calculated from Figure 10 with the aid of the gas phase transitions are gathered in Table 2 and in Figure 11, which shows the shifts against the solvent polarizability. The shifts for the transition $S_0 \rightarrow S_3$ are only evaluated down to 213 K, at lower temperatures the corresponding peak maxima are hardly recorded (Figure 10).

Absorption Spectra of Perylene. The first four 0−0 electronic transitions for perylene in an array of neon[20] at 4 K are used as references (Table 2) for assessing the perylene solvatochromism in 2MB, and those are placed at 23 883 cm^{-1} (in good accord with the corresponding data in the gas phase obtained from supersonic jet experiments, that is, at 24 058.9 cm^{-1}),[21] 34 977, 38 491, and 41 152 cm^{-1}.

Figure 12 shows the absorption spectra of perylene in 2MB ranging from 293 to 173 K. As shown in Figure 13, the solvatochromic shifts for the four transitions are plotted against the polarizability on going from perylene in a neon matrix at 4 K to perylene in a 2MB solution.

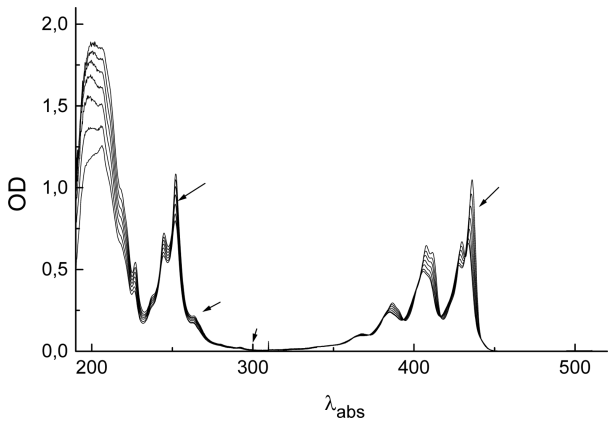


Figure 12. UV−vis absorption spectra of perylene in 2MB from 293 to 153 K. The arrows indicate the peaks taken as references to measure the solvatochromic shifts, that is, at 23 883, 34 977, 38 491, and 41 152 cm^{-1}.

On the Spectroscopic Rule Stated by Renger et al.: Solvatochromism Seemingly Increases as the Electronic State Energy of the Chromophore Increases. The theory of solvatochromism reported by Renger, Grundkötter, Madjet, and Müh was put to the test on only two molecular systems (Scheme 1), *bacteriochlorophyll a*and *bacteriopheophytin a*. These molecules are polar; their state dipole moments and transition moments have been calculated by Cory, Zerner, Hu, and Schulten[23] in 1998, using quantum mechanical electronic structure calculations performed with the aid of the intermediate neglect of differential overlap model parametrized for spectroscopy (INDO/S and INDO−CIS) methodologies. The corresponding permanent dipole moments for the S_0, S_1, and S_2 states (7.3, 2.93, and 4.52 D, respectively) are large and distinct from one another, thus involving important changes in the excited state molecular structure compared with that of the ground electronic state—these dipole moment magnitudes and orientations imply a nonrigid molecular geometry which changes on photoexcitation. The molecules *bacteriochlorophyll a* and *bacteriopheophytin a* were dissolved in 16 nonpolar solvents with increasing polarizability from *n*-pentane (n_r^2 = 1.84) to CS_2 (n_r^2 = 2.64) and 13 nonpolar solvent mixtures of hexane and CS_2 (from n_r^2 = 2.06 to n_r^2 = 2.58). The experimental data reported by Renger[11] et al., the linear fits of the experimental transition state energies E_{10} (Q_y transition) and E_{20} (Q_x transition), and the first two electronic transitions reported by Limantara[24] et al., plotted against solvent polarizability (represented by the Bayliss-McRae relationship $(n_r^2 - 1)/(2n_r^2 + 1)$), yielded the vacuum transition state energies of 13 800 (E_{10}^{vac}) and 18 363 cm^{-1} (E_{20}^{vac})[11]. Figure 14 and Figure 15 are plotted for the molecules *bacteriochlorophyll a*

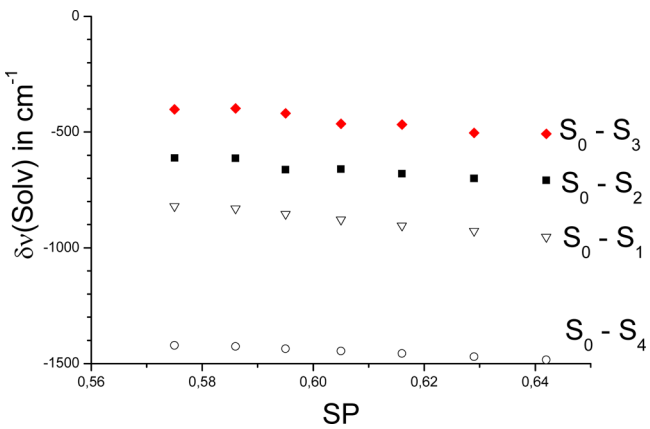


Figure 13. Solvatochromic shifts for the transitions $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$, $S_0 \rightarrow S_3$, and $S_0 \rightarrow S_4$ for perylene in 2MB solution against the solvent polarizability parameter.

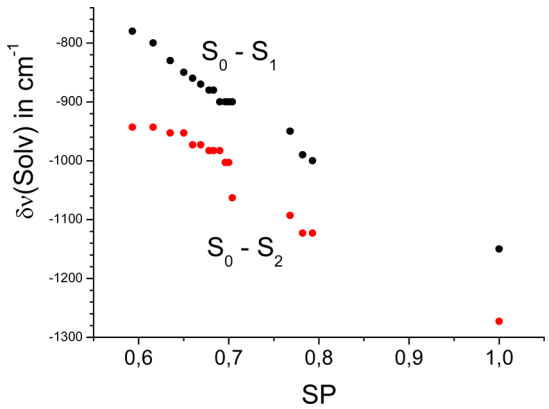


Figure 14. Solvatochromic shifts for the molecule *bacteriochlorophyll a* against the SP parameter.

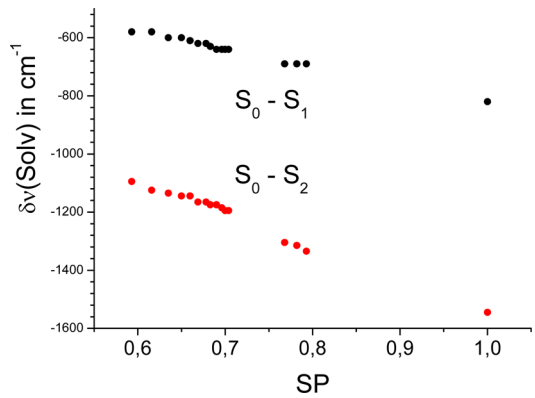


Figure 15. Solvatochromic shifts for the molecule *bacteriopheophytin a* against the SP parameter.

and *bacteriopheophytin a* by calculating the solvatochromic shifts, in Figures 3, 5, 7, 9, and 11, for the first two electronic state energies against the SP parameter. The SP parameter shows good correlation with the Lorenz−Lorentz function,[14] $f(n_r^2) = f(n_r^2) = ((n_r^2 - 1)/(n_r^2 + 2))$, as well as with the Bayliss−McRae relationship mentioned above. As a result, the solvatochromic shifts for the E_{10} state energy are smaller than those for the E_{20} state energy.

Apparently the theory of solvatochromism works well and is in accordance with Renger's rule as it is supported by Renger et al. Figures 14 and 15 seem to demonstrate that the oscillator strengths for the electronic transitions involved are not necessary, but conversely, several relevant counterexamples, which are reported in Figure 3, Figure 5, Figure 7, Figure 9, Figure 11, and Figure 13, do not validate it (vide infra). Herein, a systematic study has been presented for a series of aromatic molecules, benzene, naphthalene, anthracene, DPA, perylene, and rubrene, which is outstanding to definitively invalidate the spectroscopic rule reported by Renger et al.—a systematic study that is absent in their work.[11]

It is noteworthy to emphasize the important features exhibited by the series of aromatic molecules investigated in this paper, (1) they exhibit a rigid molecular geometry, (2) for each solute its absorption bands do not maintain a parallel increase of the intrinsic intensity (oscillator strength) of the transition as the transition energy increases, and also (3) they have sufficiently high symmetry to neglect the influence of their permanent dipole moments when the excitation energy of the electronic transition is increased.

The experimental findings reported above in Figure 3, Figure 5, Figure 9, Figure 11, and Figure 13 prove to be crucial in investigating the spectroscopic rule stated by Renger et al. From these experiments, several pieces of evidence can be extracted as follows: (1) The solvatochromism found for the transition $S_0 \rightarrow S_1$ of both benzene and naphthalene is not only very small, about −250 and −160 cm^{-1}, respectively, but it is also insensitive to the solvent polarizability, see Figure 3 and Figure 5. Consequently, this solvatochromism indicates that no significant change is generated in the polarizability of benzene and naphthalene upon photoexcitation to the first singlet excited state, while the energy of these molecules has not kept constant but it has been increased by 38 567 and 33 333 cm^{-1}, respectively. (2) The solvation energy for the $S_0 \rightarrow S_3$ transition of DPA is much smaller than that for the $S_0 \rightarrow S_2$ transition, and is of similar value to that of the $S_0 \rightarrow S_1$ transition, Figure 9, while its electronic transitions increase their energies to 26 273 ($S_0 \rightarrow S_1$), 40 343 ($S_0 \rightarrow S_2$), and 45 129 cm^{-1} ($S_0 \rightarrow S_3$). (3) The state S_3 of rubrene shows the same behavior as that described in point 1, as can be seen in Figure 11; its solvatochromism is small and insensitive to solvent polarizability. (4) The solvation energies for perylene increase following this order $S_0 \rightarrow S_3 < S_0 \rightarrow S_2 < S_0 \rightarrow S_1 < S_0 \rightarrow S_4$ (Figure 13); that is, they do not follow what is predicted by the spectroscopic rule by Renger et al.

As a matter of fact, the above-mentioned piece of evidence makes the spectroscopic rule proposed by Renger et al. unacceptable.

On Solvatochromism and Its Independence of the Oscillator Strength of the Transition Moment. The above-mentioned evidence pointing to the inadequacy of the rule of Renger et al. is in accordance with a significant decrease in the intrinsic intensity of the transition (Table 1) that does not follow the increase of the corresponding excitation energy. It is particularly revealing that very small solvatocromic values match very small values of the extinction coefficient of the transition, for instance, the behavior shown by the $S_0 \rightarrow S_1$ transition of benzene and naphthalene, Table 1. From this evidence it can be inferred that, as indicated by Longuet-Higgins and Pople, high intensities help increase solvatochromism, and as a matter of fact, this can be supported by the above-mentioned evidence.

■ CONCLUSION

It seems to be supported that any electronic excitation can lead to greater electron delocalization that generates an increase of the polarizability of the system, thus increasing the red shift due to the medium polarizability. But to generalize that this increase of the red shift will continue to rise with increasing excitation energy from this is excessive; several counterexamples are introduced herein. We have not found any exception, however, for the following rule: "It will be hard to find an aromatic molecule that on Franck−Condon excitation generates an electronic excited state of lower polarizability than that of the ground electronic state."

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Notes

The authors declare no competing financial interest.

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