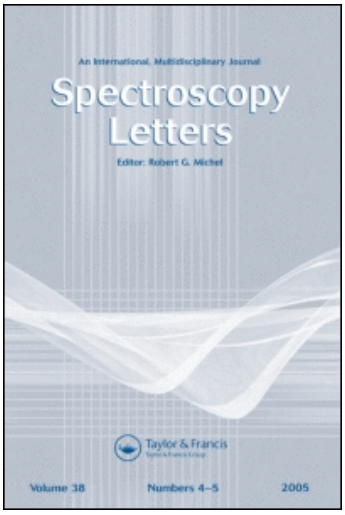

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Modification of the Perov-Bakhshiev's Frequency Shift Formula and the Extension of its Applicability Field

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To cite this Article Haba, M.(1986) 'Modification of the Perov-Bakhshiev's Frequency Shift Formula and the Extension of its Applicability Field', Spectroscopy Letters, 19: 9, 965 — 979
To link to this Article: DOI: 10.1080/00387018608069302
URL: http://dx.doi.org/10.1080/00387018608069302

SPECTROSCOPY LETTERS, 19(9), 965-979 (1986)

MODIFICATION OF THE PEROV-BAKHSHIEV'S FREQUENCY SHIFT FORMULA AND THE EXTENSION OF ITS APPLICABILITY FIELD

Key Words : UV/VIS-spectra; Solvent effects; Binary solutions; Local field models; Nitranilines; Nitrophenols; Nitrosonaphtols

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ABSTRACT

Starting from the Perov-Bakhshiev's frequency shift formula and using an analogy from electronics a new frequency shift formula was deduced which gives the possibility of describing the spectral shift effects in the electronic spectra observed at a great variety of the spectral-active compounds dissolved in various non-polar and polar solvents with universal or specific solvation effects.

0038-7010/86/1909-0965$3.50/0

INTRODUCTION

For the description of the frequency shifts in the electronic absorption and fluorescence spectra of the ideal binary spectral-active solutions a simple statistical model was proposed[1] which consists of one molecule of the solute u and Z molecules of the surrounding solvent v. In connection with this model it was presumed that the electronic transitions of the solute molecule follow the Franck-Condon principle both in absorption and in fluorescence and the pair interactions between the solute molecule and the solvent molecules are universal interactions of dispersion, induction and orientation type, which can be described with additive potentials of London, Debye and Keesom type. On this basis it was shown that the spectral shift $\Delta\nu_v^{a,f} = \nu_0^{a,f} - \nu_v^{a,f}$, which occurs, on the wave numbers scale, in the position of the absorption (a) or fluorescence (f) spectrum of the pure electronic transition of the solute molecule, when it passes from the isolated state or vapour phase (o) to the solution phase (v), can be expressed as a function of the polarity parameters of the solute and solvent molecules by a relation of the form :

$$hc\Delta\nu_v^{a,f} = \sum_z \frac{1}{r_{uvz}^6} \left\{ \alpha_u^o (\mu_{vz}^o)^2 + \frac{3}{2} \alpha_u^o \alpha_{vz}^o \frac{I_u^o I_v^o}{I_u^o + I_v^o} - \right. \tag{1}$$

$$\left. - \alpha_u^i (\mu_{vz}^o)^2 - \frac{3}{2} \alpha_u^i \alpha_{vz}^o \frac{I_u^i I_u^o}{I_u^i + I_{vz}^o} + ((\mu_u^o)^2 - \right.$$

$$-(\mu_u^i)^2)\alpha_{vz}^o \pm \frac{2}{3}(\mu_{vz}^o)^2((\mu_u^{o,i})^2 - \mu_u^i \mu_u^o \cos\varphi)\Big\}.$$

In this relation α, μ and I are the polarizability, the dipole moment and the ionization potential of the considered molecule , respectively; r_{uvz} is the distance between the u molecule and the v molecules, φ - the angle between the vectors $\vec{\mu}_u^o$ and $\vec{\mu}_u^i$ and z a summing index.

Since formula (1) is not adequate in the previous form for analyses and practical applications we tryed to obtain a new form for it that would be easier to be interpreted and handled and also to extend its applicability field.

THEORY AND DISCUSSION

1. We presume that the Z solvent molecules which take part effectively in solvation of the solute molecule, thus forming a solvation shell around it, are identical between them with regard to their basis parameters, varying only the distance r_{uvz} between them and the central solute molecule. In these conditions, using the notations:

$$1/\rho_{uv}^6 = (1/Z)\sum_z (1/r_{uv}^6)_z \qquad (2)$$

$$1/I_{uv}^{o,i} = 1/I_u^{o,i} + 1/I_v^o \qquad (3)$$

and grouping conveniently the terms of relation (1), we obtain the spectral shift formula[2] :

$$hc\Delta\nu_v^{a,f} = (A_{uv}^{a,f}\,\alpha_v^o + B_{uv}^{a,f}(\mu_v^o)^2/3kT)Z/\rho_{uv}^6 \qquad (4)$$

where

$$A_{uv}^{a,f} = (\mu_u^i)^2 - (\mu_u^o)^2 + 3(\alpha_u^i I_{uv}^i - \alpha_u^o I_{uv}^o)/2 \qquad (5a)$$

$$B_{uv}^{a} = 2\mu_u^o(\mu_u^i\cos\varphi - \mu_u^o) + 3kT(\alpha_u^i - \alpha_u^o) \qquad (5b)$$

$$B_{uv}^{f} = -2\mu_u^i(\mu_u^o\cos\ - \mu_u^i) + 3kT(\alpha_u^i - \alpha_u^o) \qquad (5c)$$

As it can seen, in this formula there explicitly appear all the factors on which, in this case, the spectral shifts depend, namely the number of the solvating molecules, the harmonical mean of the sixth order of the intermolecular distances, the temperature of the surrounding medium and the microscopical polarity parameters of the intreracting molecules. From this formula results a series of consequences which of we shall enumerate the following :

- The formula (4) may also be applied on a binary solution consisting of N spectral-active molecules independent among themselves. If in this sistem Z fluctuates from one u-molecule to another, then it is necesary, in order to preserve the relation (4), to replace in it the terms Z/ρ_{uv}^6 with $N/R_{uv}^6 = \sum_n Z_n/\rho_{uvn}^6$ and $\Delta\nu_v^{a,f}$ with $\overline{\Delta\nu}^{a,f} = (\sum_n \Delta\nu_{vn}^{a,f})/N$.

- For a series of the u solutions obtained with nonpolar solvents (N) having identical or nearly identical ionization potentials and molecular radiuses, the corresponding spectral shifts $\Delta\nu_N^{a,f}$ are directly propor-

tional to the polarizabilities α_N^o. When the molecular radiuses are not identical, then $\Delta\nu_N^{a,f}$ is directly proportional to the sizes $\alpha_N^o/\varrho_{uN}^6$.

- Replacing in the previous series every nonpolar solvent (N) with a polar homologous (P) results, for supplimentary spectral shift : $\delta\nu_{P\backslash N}^{a,f} = \Delta\nu_P^{a,f} - \Delta\nu_N^{a,f}$, the proportionality $\delta\nu_{P\backslash N}^{a,f} = \text{const.}(\mu_P^o)^2$. If $A_{uP}^{a,f}/\varrho_{uP}^6 \neq A_{uN}^{a,f}/\varrho_{uN}^6$, then $\delta\nu_{P\backslash N}^{a,f}$ depend liniarly on $(\mu_P^o)^2/\varrho_{uP}^6$.

- When, during the electronic transition the polarirability and the dipole moment of a spectral-active molecule display additive and multiplicative variations, respectively, that is :

$$\alpha_u^i = \alpha_u^o + \alpha \tag{6a}$$

and

$$\mu_u^i = m\,\mu_u^o \tag{6b}$$

then the constants $A_{uv}^{a,f}$ and $B_{uv}^{a,f}$, expressing the sensibility of the considered spectra to the parameters α_v^o and $(\mu_v^o)^2$, satisfy relations of the form :

$$A_{uv}^{a,f} = a_{1v}^{a,f}\,(\mu_u^o)^2 + a_{2v}^{a,f}\,\alpha_u^o + a_{3v}^{a,f} \tag{7a}$$

$$B_{uv}^{a,f} = b_{1v}^{a,f}\,(\mu_u^o)^2 + b_{2v}^{a,f} \tag{7b}$$

We have experimentally established[3] that a relation of the form (7b) is valid for the position isomers of nitranaline dissolved in polar solvents.

If the approximations : $\alpha_u^i \simeq \alpha_u^o$ and $I_u^i \simeq I_u^o$ are valid, then $B_{uv}^{a,f} = K^{a,f}\,A_{uv}^{a,f}$, where $K^{a,f}$ is a proportionality coefficient.

2. An important shortcoming of the formula (4) and its analogs consists in the fact that, being composed of microscopical sizes, it does not permit a direct comparision with the usual shift formulas expressed in terms of the refractive index n_v and the dielectric constant ε_v of the solvents.

In order to remove this impediment we accept futhermore that the vicinity of the dissolved molecule can be defined by the relation[2] :

$$\rho_{uv} \simeq \sqrt[6]{Z\, r_u^3\, r_v^3} \leq r_u + r_v \qquad (8a)$$

and the solvent lying in this vicinity can be considered as a dielectric continuum characterized, in a first approximation, in keeping with Lorentz-Debye's model for polarization, by the specific molecular refraction

$$[n^2]_v = (n_v^2 - 1)/(n_v^2 + 2) = \alpha_v^0/r_v^3 \qquad (8b)$$

and by the specific molecular polarization

$$[\varepsilon]_v = (\varepsilon_v - 1)/(\varepsilon_v + 2) = (\alpha_v^0 + (\mu_v^0)^2/3kT)/r_v^3 =$$

$$= [n^2]_v + (\mu_v^0)^2/3kT\, r_v^3 \qquad (8c)$$

In these expressions r_u and r_v are the radiuses of the u and v molecules, respectively.

By introducing these expressions in Eq.(4) we obtain the spectral shift formula[2] :

$$hc\, \Delta\nu_v^{a,f} = \tilde{A}_{uv}^{a,f}\, [n^2]_v + \tilde{B}_{uv}^{a,f}\, [\varepsilon\, n^2]_v \qquad (9)$$

where $\tilde{A}_{uv}^{a,f} = A_{uv}^{a,f}/r_u^3$, $\tilde{B}_{uv}^{a,f} = B_{uv}^{a,f}/r_u^3$ and $[\varepsilon \backslash n^2]_v = [\varepsilon]_v - [n^2]_v$.

As it can be seen, this formula is very similar with McRae's[4] or Bakhshiev's[5] usual formulas, From (9), by adequate particularizations, other usual spectral shift formulas, can be found, for example the formulas of Bayliss[6], Weljkcovič[7] or Suppan[8].

3. Formulas (4) and (9) can also be extended to such binary solutions in which exist not only universal interactions but also specific ones, for example donor - acceptor or hydrogen bond type interactions. If these interactions can be described in a first approximation by additive potentials, then we can write the following expression for the spectral shifts :

$$hc\,\Delta\tilde{\nu}_v^{a,f} = \tilde{A}_{uv}^{a,f}\,[n^2]_v + \tilde{B}_{uv}^{a,f}\,[\varepsilon\backslash n^2]_v + \tilde{C}_{uv}^{a,f} \qquad (10)$$

where the term $\tilde{C}_{uv}^{a,f}$ is independent from the sizes $[n^2]_v$ and $[\varepsilon \backslash n^2]_v$ and it generally varies from a solvent to another. For a class of similar solvents $\tilde{C}_{uv}^{a,f}$ is a constant.

We have experimentally established that a relation of the form (10) is valid for the position isomers of nitranaline[3,9] and nitrophenol[10], dissolved in a great variety of nonpolar and polar solvents. On this occasion we have found that the various solvents may be classified in the following categories : nonpolar nonspecific ($[\varepsilon\backslash n^2] = 0$, $\tilde{C}_{uv}^{a,f} = 0$), nonpolar specific ($[\varepsilon\backslash n^2] = 0, \tilde{C}_{uv}^{a,f} \neq 0$),

polar nonspecific ($[\varepsilon \backslash n^2] \neq 0$, $\tilde{C}_{uv}^{a,f} = 0$) and polar specific ($[\varepsilon \backslash n^2] \neq 0$, $C_{uv}^{a,f} \neq 0$) solvents. However, a more exact treatment of the concomitent manifestation of the universal and specific solute-solvent interactions needs to take into account more perfected statistical models, for example, the Perov's model[11].

4. Relations (4) and (9) can also be perfected concerning the description of the universal interactions. For example, if, in formula (1) we use, instead of the vacuum pair interaction potentials $U_{uv(vac.)}$, the corected potentials $U_{uv(sol)} = \varphi U_{uv(vac.)}$, where φ is a 'correcting' factor, then we find a shift formula of the form:

$$hc\Delta\nu_v^{a,f} = \bar{Z}\,\bar{\varphi}\,(A_{uv}^{a,f}\alpha_v^o + B_{uv}^{a,f}(\mu_v^o)^2/3kT)/r_{uv}^6 \qquad (11)$$

Here $\bar{Z}$ is, according to Lutzkiy and coworkers[12], the mean of $\bar{Z}$ after all dipole configurations; $\bar{\varphi}$ is the mean of φ after all dipole configurations, all molecular vicinities and all various energetic terms ; r_{uv} is $r_u + r_v$. This formula differs from formula (4) only by the factor $\bar{Z}\,\bar{\varphi}/r_{uv}^6$. If in (4) we replace Z with $\bar{Z}$ and ϱ_{uv} with r_{uv}, then the two formulas become identical.

5. A further development of formulas (4) and (9) can be obtained by replacing in them the parameters α_v^o, μ_v^o and $[n^2]_v$, $[\varepsilon]_v$, respectively, with the parameters

$$\alpha_v = \alpha_v^o/(1-2\,\beta_\alpha\,\alpha_v^o/r_v^3) \qquad (12a)$$

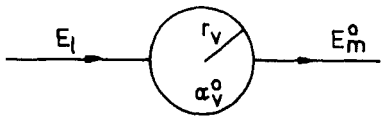
$$\mu_v = \mu_v^o/(1-2\,\beta_\alpha\,\alpha_v^o/r_v^3) \qquad (12b)$$

$$(n^2)_v = [n^2]_v/(1-2\,\beta_n[n^2]v) \qquad (12c)$$

$$(\varepsilon)_v = [\varepsilon]_v/\,(1-2\,B_\varepsilon\,[\varepsilon]_v) \qquad (12d)$$

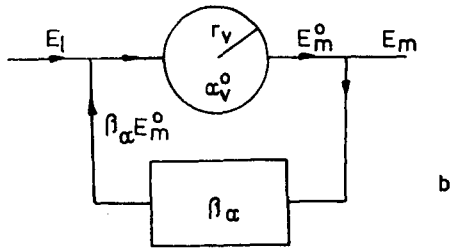
Here β_α , β_n and β_ε are „reaction" factors which take into account the influence of the surrounding molecules on the considered solvent molecule.

For deduction of these relations we use an analogy from electronics. Namely, we accept that every molecule of a nonpolar or polar solvent behaves, in a first approximation, as an off-line field amplifier (Fig.1a) having as amplifying factor the size $2\,\alpha_v^o/r_v^3$ and in a second approximation as an on-line field amplifier (Fig.1b) having as amplifying factor the size $2\,\alpha_v/r_v^3$.



a

$$E_m^o = \frac{2\alpha^o}{r_v^3}E_l$$



b

$$E_m = \frac{2\alpha_v^o}{r_v^3}(E_l + \beta_\alpha E_m^o) = \frac{2\alpha_v}{r_v^3}E_l$$

Figure 1. Local field model

As input size for this amplifier serves the local electric field E_l that realy acts on the investigated molecule and as output size serves the electric field E_m^o or E_m corresponding to the induced dipole moment $m_v^o = \alpha_v^o E_l$ or $m_v = \alpha_v E_l$. Since $E_m = 2\alpha_v^o(E_l + \beta_\alpha E_m^o)/r_v^3 = 2\alpha_v E_l/r_v^3$ results that $\alpha_v = \alpha_v^o/(1-2\beta_\alpha \alpha_v^o/r_v^3)$. In this way we obtain (12a). Combining (12a) with (8b) and putting $\beta_\alpha = \beta_n$ we obtain (12c). If the isolated solvent molecule has also a permanent dipol moment μ_v^o, then by its surrounding with other molecules this dipole moment will be modified in the same way as the induced dipole moment m_v^o with the factor $1/(1-2\beta_\alpha \alpha_v^o/r_v^3)$. So we obtain the actual permament dipole moment μ_v defined by (11b). To this dipole moment corresponds, due to the thermal agitation of the molecules, the orientation polarizability $\alpha_v' = (\mu_v)^2/3kT$. Therefore, replacing in (8c) the expression $\alpha_v^o + (\mu_v^o)^2/3kT$ with the expression $\alpha_v + \mu_v^2/3kT$ and using the notation :

$$\beta_\varepsilon = \frac{1}{2[\varepsilon]_v}\left(1 - \frac{[\varepsilon]_v(1-2\beta_n[n^2]_v)^2}{[\varepsilon]_v - 2\beta_n[n^2]_v^2}\right) \qquad (13)$$

we obtain (12d).

From (13), which gives an approximate correlation between β_ε and β_n, results that, excepting the case $\beta_n = [\varepsilon]/2[n^2]^2$, when β_ε is undefined, β_ε can generally be greater, equal or less than 0 as β_n is greater, equal or less than $1/[n^2] - 1/2[\varepsilon]$. However, because

the majority of the usual liquids have $[n^2] = 0.2 \div 0.4$ and $[\varepsilon] = 0.2 \div 1.0$ results as a rule : $\beta_n \geqslant 0$ and $\beta_\varepsilon \geqslant 0$ (positive reaction). It can also be seen that if $0 \leqslant \beta_n \leqslant 1/2\,[n^2]$ then $0 \leqslant \beta_\varepsilon \leqslant 1/2[\varepsilon]$, too.

These conclusions agree with the theories refering to the polarization of the liquid dielectrics. For example, in Onsager's theory[13] $\beta_n^0 = [n^2]/(1+[n^2])$ and $\beta_\varepsilon^0 = [\varepsilon]/(1+[\varepsilon])$. In Wertheim's theory[14]

$$\beta_{n,\varepsilon}^W = \beta_{n,\varepsilon}^0 + \frac{17}{52}(\beta_{n,\varepsilon}^0)^2 + \frac{509}{64}(\beta_{n,\varepsilon}^0)^3 + \ldots > \beta_{n,\varepsilon}^0 \qquad (14)$$

and this expression tends to the value 4, instead of 1/2, when $[n^2]$ and $[\varepsilon]$, respectively, tend to the value 1. In other theories β_n and β_ε have other values.

However, at the evaluation of the value and the sign of the reaction factors we also must have in view that non all of solvent molecules, lying in the vicinity of the dissolved molecule, are symmetrically surrounded by molecules of the same kind and therefore the real values of β_n and β_ε can be very different from those which are resulting from the mentioned theories.

On the basis of the presented facts the relation (10) may be written under the form :

$$hc\Delta\nu_v^{a,f} = \tilde{A}_{uv}^{a,f} \frac{[n^2]_v}{1-2\,\beta_n[n^2]_v} - \tilde{B}_{uv}^{a,f}\left(\frac{[n^2]_v}{1-2\,\beta_n[n^2]_v} - \frac{[\varepsilon]_v}{1-2\,\beta_\varepsilon[\varepsilon]_v}\right) + \tilde{C}_{uv}^{a,f} \qquad (15)$$

Hence it results that by an adequate choice of the sensibility factors $\tilde{A}_{uv}^{a,f}$, $\tilde{B}_{uv}^{a,f}$ and $\tilde{C}_{uv}^{a,f}$ and the reaction factor β_n and β_ε from relation (15) other shift formulas can also be derived.

For example, if we assume that $\beta_n = 1/2(1+[n^2])$ and $\beta_\varepsilon = [n^2]/2[\varepsilon](1+[n^2])$ and neglect the term $\tilde{C}_{uv}^{a,f}$, then we obtain the shift formula :

$$hc\Delta\nu_v^{a,f}=(1+[n^2]_v)(A_{uv}^{a,f}[n^2]_v + B_{uv}^{a,f}[\varepsilon\backslash n^2]_v \qquad (16)$$

which gets, with the usual approximations $\alpha_u^i \simeq \alpha_u^o$ and $I_u^i \simeq I_u^o$, into Bakhshiev's formula[5]. Choosing $\beta_n = 0$ and $\beta_\varepsilon = 1/2$ results a shift formula of the form :

$$hc\Delta\nu_v^{a,f} = \tilde{A}[n^2] + \tilde{B}\varepsilon + \tilde{C} \qquad (17)$$

which shows a linear dependence of spectral shifts from the dielectric constant ε. Such a formula is experimentally established by us in[15] for the spectral shifts observed at nitrosonaphtols in alcohols. For $\tilde{A}_{uv}^{a,f} \simeq 0$, $\tilde{C}_{uv}^{a,f} = 0$, $\beta_n=(1-[n^2])/4$ and $\beta_\varepsilon=(1-[\varepsilon])/4$ results a shift formula of the form :

$$hc\Delta\nu_v^{a,f}= 2\tilde{B}_{uv}^{a,f}([\varepsilon]/(1+[\varepsilon])-[n^2]/(1+[n^2])) \qquad (18)$$

which was used in[17] for the description of the spectral shifts observed in the case of hidrogen bond molecular complexes.

However, the deduction from (15) of some usual formulas requires an individual treatment of the energetic

terms which correspond to various universal interactions that exist in the considered molecular system and a selection of some particular values for the corresponding reaction factors. This is explicable, considering that the corresponding polarizabilities are generally different from one another. For example, the finding of the usual McRae's formula[4] :

$$hc\Delta\nu = 2\,\tilde{A}\,[n^2]/(1 + [n^2]\,) + \tilde{B}[\varepsilon\backslash n^2] \quad (19)$$

in which the term corresponding to quadratic Stark's effect was neglected, implies the identification of β_n in the first term of relation (15) with the value $\beta_{nI} = (1- [n^2]\,)/4$ and in the second term with the value $\beta_{nII} = \beta_\varepsilon = 0$. On the contrary, finding of the Bilot - Kawsky's formula[16] needs to choose the following values: $\beta_{nI} = 1/2(2+ [n^2]\,)$, $\beta_{nII} = 1/2(1+ [n^2]\,)$ and $\beta_\varepsilon = [n^2]/2[\varepsilon]\,(1+[n^2]\,)$. If we choose the values $\beta_{nI} = \beta_{nII} = (1 - [n^2]\,)/4$ and $\beta_\varepsilon = 1/2[\varepsilon]\,(2+[\varepsilon]\,)$, then we find a shift formula of the form :

$$hc\Delta\nu_{\nu}^{a,f} = 2\tilde{A}\,\frac{[n^2]}{1+[n^2]} + \tilde{B}[\varepsilon] + \tilde{D}\,\frac{(1+[\varepsilon]\,)}{1+[\varepsilon]- 2[\varepsilon]^2} + \tilde{C} \quad (20)$$

Such a formula was experimentally established in[18] for antracen and antracen derivatives dissolved in various nonpolar and weakly polar solvents.

CONCLUSIONS

Synthetizing the results of this work we can say

that the Perov-Bakhshiev's formula in our variant (15) gives the possibility of describing the spectral shift effects in the electronic spectra observed at a great variety of the spectral-active compounds dissolved in various nonpolar and polar solvents which display or not complexing effects.

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Date Received:
Date Accepted: