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Solvent Effect on the Excited Charge Transfer State of Naphthylamine Sulfonate Derivatives: Steady State and Time resolved studies

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Abstract

Solvent effect on the absorption and fluorescence emission spectra of 1-naphthylamine-4-sulfonate (1NA4S) and 2-naphthylamine-6-sulfonate (2NA6S) were investigated. Excited state fluorescence decay measurements were also measured in different solvents. The spectral shifts are well correlated with several multiparametric relationships that predict the participation hydrogen bonding interactions (specific) versus non-hydrogen bonding interactions (non-specific) on the photophysical properties. Kamlet-Taft with their three parametric relationship which was then improved by Catalán by splitting the π^* (dipolarity/polarizability) to parameters namely, solvent's polarizability) solvent's dipolarity, and very recently Laurence relationships. The three-parameter relationship by Kamlet-Taft has shown that the absorption energy is mainly controlled by specific interactions while the emission energy is controlled by the non-specific interactions. On the other hand, Catalán's treatment has shown that non-specific interaction has higher contribution to the emission energy than predicted by Kamlet-Taft treatment. Laurence's treatment has shown that hydrogen bonding interaction has higher contribution than non-hydrogen bonding interactions to the emission energy for both compounds while they contribute equally to their absorption energy.

Keywords: solvent effect; fluorescence; intramolecular charge transfer; intramolecular proton transfer.

Introduction

Study of intramolecular charge transfer (ICT) phenomenon has attracted the attention of many studies [1] over the last few decades. Recent review article by Bureš [1], has presented the effect of chemical structure on the photophysical characteristics of ICT compounds and tuning of these properties by proper design of the fluorophores. ICT compounds are characterized by the existence of an electron-donating and electron withdrawing moieties linked by π-bridge (D-π-A). Research interests in ICT systems are also extended for the study of molecular systems having an intermolecular charge transfer excited state but greatly influenced by specific interactions [2-10]. For molecular systems with excited state intramolecular charge transfer (ESICT) phenomenon, in most cases the observed dual emission arises from the locally (LE) and intramolecular charge transfer (ICT) states. Józefowicz et al. have reported dual fluorescence from the ICT state and hydrogen bonded ICT state in case of one of dimethylaminonaphthalene derivatives

called Laurdan (6-dodecanoyl-2-dimethylaminonaphthalene) [4].

It has been reported that aromatic systems with electron-acceptor substituents are capable of forming stronger hydrogen bonding (HB) in the excited state than that observed in the ground state [11-14], and the increased HB in the excited state led to stabilization of the ICT state [13, 15, 16].

The presence of the amino group on the naphthalene ring has considerable effect on its absorption spectrum. In contrast to the observed dual fluorescence from the LE and ICT states for 1-amino-4-cyanonaphthalene and 1-(dimethylamino)-4-cyanonaphthalene [17-19]; replacement of the amino substituent by azetidinyl group was found to reduce the dual fluorescence from a charge transfer (CT) state [20]. *N,N*-dimethyl-1-aminonaphthalene was reported as a novel molecule with HB interactions in both the ground and the excited states [21-29].

It has been reported that N-phenyl derivatives of some naphthalimides exhibit higher internal conversion to the ground state than the corresponding N-alkyl derivatives [30-33]. It has also been reported

that the ICT emission comes from the planar configuration that makes ICT state more stabilized than the LE state [34].

In this work we extend our studies of the effect of solvents on the intramolecular charge transfer process, for 1-aminonaphthalene-4- sulfonate (1NA4S) and 2- aminonaphthalene-6- sulfonate (2NA6S). Photophysical properties of both compounds were studied in different solvents and the obtained data are correlated to different solvent polarity parameters. Different multilinear regression relationships were used to evaluate the contribution of hydrogen bond donation and hydrogen bond acceptance properties of the solvents versus the polarity/polarizability interactions to their photophysical properties.

Experimental:

1-naphthylamine-4-sulfonate (1NA4S) and 2-Naphthylamine-6-sulfonate (2NA6S) and were obtained from Aldrich and their sodium salts were recrystallized twice from ethanol. Organic solvents used in this study such as ethanol (EtOH), methanol (MeOH), 1-butanol (1BuOH), 2-propanol (PrOH), iso-butanol (iBuOH), tetrahydrofuran (THF), acetonitrile (ACN), ethylacetate, (EtAc), dimethylsulfoxide (DMSO) and dimethylformamide (DMF) were from Sigma-Aldrich of highest purity

grade. Concentrations of 2NA6S and 1NA4S were around 6 x 10^{-5} M. UV-1900 UV-VIS Spectrophotometer was used for absorption spectra collection while RF-6000 Spectrofluorophotometer was used for fluorescence emission measurements. Quinine sulfate in 1N H_2SO_4 was used as the standard for the determination of the fluorescence quantum yields [40] according to Eq(1):

$$\Phi_u = \left(\frac{F_u}{A_u}\right)\left(\frac{A_s}{F_s}\right)\left(\frac{n_u^2}{n_s^2}\right)\Phi_s \qquad (1)$$

where A_u is the absorbance of the sample and A_s is the absorbance of the standard, F_s is the standard's area of the fluorescence spectrum and F_u is the sample's area of the fluorescence spectrum, n_u is the refractive index of the unknown's solvent and n_s is the standard's solvent and Φ_s is the fluorescence quantum yield of the standard.

Easylife from Optical Building Blocks was used the fluorescence lifetime measurements. The excitation source was 340 nm LED. Fluorescence decay was found to fit with biexponential function (Eq. 2), with χ^2 of about 1.0±0.1.

$$I(t) = a_1\, exp\left(\frac{-t}{\tau_1}\right) + a_2\, exp\left(\frac{-t}{\tau_2}\right) \qquad (2)$$

Table 1. Photophysical data of 1NA4S in different solvents and solvent polarity parameters

	Solvent	λ_a^{max}	λ_f^{max}	a_1	τ_1, ns	a_2	τ_2, ns	χ^2	Φ_f	$f(\varepsilon,n)$	$\phi(\varepsilon,n)$	E_T^N
1	Water	319	418	64.4	9.0	35.6	22.1	1.06	0.89	0.913	0.910	1.000
2	Methanol	330	406	92.6	6.2	7.4	24.2	1.1	0.88	0.855	0.875	0.762
3	Ethanol	330	405	93.1	6.4	6.9	25.0	1.2	0.80	0.813	0.898	0.654
4	2-Propanol	327	406	90.5	6.8	9.5	23.8	1.2	0.90	0.765	0.896	0.546
5	Iso-butanol	328	406	90.1	7.2	9.9	24.8	1.1	1.0	0.703	0.999	0.552
6	1-Buthanol	330	406	90.0	7.0	10.0	24.0	1.2	1.0	0.753	0.919	0.586
7	Ethylacetate	332	401	95.7	5.4	4.3	25.6	1.2	0.73	0.489	0.751	0.228
8	Acetonitrile	331	407	92.6	6.2	7.4	24.0	1.2	0.75	0.863	0.900	0.46
9	Tetrahydrofuran	334	403	94.4	5.7	5.6	24.0	1.1	0.65	0.547	0.826	0.207
10	Dimethylformamide	336	410	84.5	7.8	15.5	22.8	1.1	1.0	0.836	1.002	0.386
11	Dimethyl sulfoxide	336	415	74.9	8.6	25.1	22.7	1.2	1.0	0.841	1.069	0.444

Table 2: Photophysical data of 2NA6S in different solvents

	Solvent	λ_a^{max}	λ_f^{max}	a_1	τ_1, ns	a_2	τ_2, ns	χ^2	Φ_f
1	Water	337	416	54.1	8.2	45.9	23.0	1.16	0.58
2	Methanol	343	405	90.6	7.1	9.4	22.9	1.24	0.36
3	Ethanol	343	404	90.4	7.7	9.6	24.8	1.19	0.35
4	2-Propanol	342	403	88.4	8.1	11.6	23.9	1.14	0.38
5	Iso-butanol	342	405	86.9	7.7	13.1	22.7	1.26	0.40
6	1-Buthanol	343	403	88.0	7.8	12.0	23.6	1.25	0.43
7	Ethylacetate	345	403	93.2	6.7	6.8	24.8	0.96	0.41

8	Acetonitrile	346	400	93.7	6.5	6.3	23.1	1.17	0.32
9	Tetrahydrofuran	348	400	93.8	6.7	6.2	23.9	1.20	0.44
10	Dimethylformamide	351	406	77.32	8.75	22.68	23.26	1.02	0.47
11	Dimethyl sulfoxide	352	410	59.75	9.97	40.25	23.96	1.18	0.48

Results and Discussion

Figs. 1 and 2 show the normalized structureless absorption and fluorescence spectra of 1NA4S and 2NA6S in a variety of solvents and their wavelengths of maximum absorption and fluorescence emission are given in Tables 1 and 2. It has been found that the absorption peaks are slightly shifted to longer wavelengths as the solvent polarity increases. It has also been observed that the bathochromic shift in the corresponding fluorescence emission peaks with the solvent polarity is slightly higher than that observed for the absorption spectra of the two compounds which reflects the slightly higher excited state dipole moment than that of the ground state.
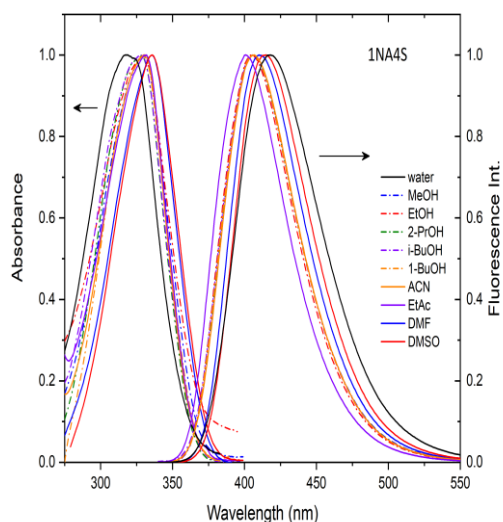

Fig. 1. Normalized absorption and fluorescence emission spectra of 5µM 1NA4S in different solvents

In contrast to our previously reported weak solvent dependent absorption spectra and pronounced fluorescence emission spectra of D-π-A compounds [2, 6-10], 1NA4S and 2NA6S show weak limited solvatochromic bathochromic shift as the polarity of the solvents increases for both absorption and fluorescence emission maxima. However, 1NA4S shows larger Stokes shift than 2NA6S in most solvents.

Figs. 3 and 4 show the time resolved fluorescence emission of 1NA4S and 2NA6S. Time resolved fluorescence decay of both compounds were found to

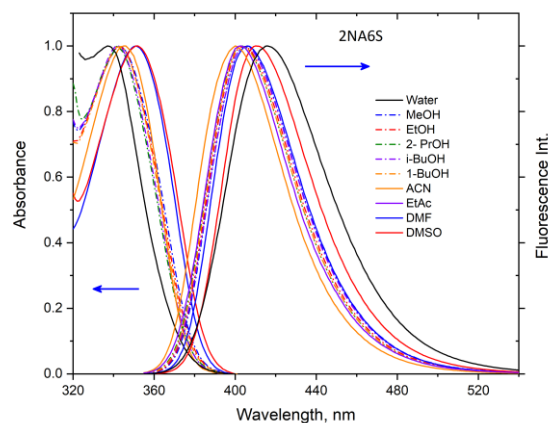fit well with biexponential function (Eq. 2) in all solvents.

Fig. 2. Normalized absorption and fluorescence emission spectra of 5µM 2NA6S in different solvents

The obtained amplitudes, a_1 & a_2, and their corresponding excited state lifetimes, t_1 & t_2, in variety of solvents are combined in Tables 1 and 2.

The obtained fluorescence lifetimes, τ_i, and their corresponding amplitudes, a_i, indicate that the fluorescence emission is attributed to the emission from LE and ICT states. Józefowicz et al. assigned the long decay component to the ICT excited state, whereas the short decay component was for LE excited state [4].
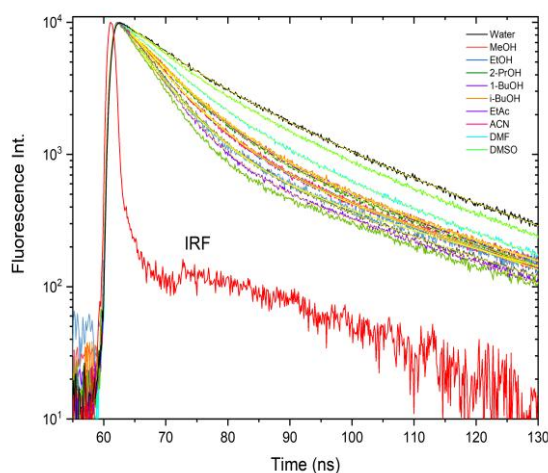

Fig. 3: Fluorescence emission decay of 1NA4S in different solvents (fit=yellow line). IRF=instrument response file
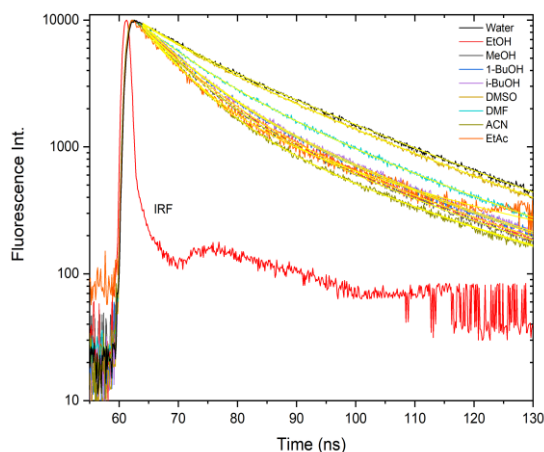
Fig. 4: Fluorescence emission decay of 2NA6S in different solvents (fit=yellow line). IRF=instrument response file

Ground and excited state dipole moments were evaluated using the absorption, ν_a, and emission, ν_e, energies according to the following correlations [41]:

$$\Delta\nu = \nu_a - \nu_e = S_1.f(\varepsilon,n) + \text{const.} \qquad (3)$$

$$\Sigma\nu = \nu_a + \nu_e = -S_2.\phi(\varepsilon,n) + \text{const.} \qquad (4)$$

where

$$\phi(\varepsilon,n) = f(\varepsilon,n) + 2g(n) \qquad (5)$$

$$S_1 = 2(\mu_e - \mu_g)^2/hca^3 \qquad (6)$$

$$S_2 = 2(\mu_e^2 - \mu_g^2)/hca^3 \qquad (7)$$

where μ_g and μ_e are the ground and excited state dipole moments, respectively. ε is the dielectric constant of the solvent and n being the corresponding refractive index. h is the Planck's constant, a is the Onsager cavity radius of the solute (6 Å, [4]), and c is the speed of light in vacuum, respectively. The solvent parameters $f(\varepsilon,n)$ and $\phi(\varepsilon,n)$ (Eq. 5) given by Bilot and Kawski [42, 43] are simplified to be:

$$f(\varepsilon,n) = \frac{2n^2+1}{n^2+2}\left(\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right) \qquad (8)$$

$$\varphi(\varepsilon,n) = \frac{2n^2+1}{n^2+2}\left(\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right) + 3\left(\frac{n^4-1}{(n^2+2)^2}\right) \qquad (9)$$

If the ground and excited states dipole moments are parallel, then Eqs. 6 and 7 can be rearranged to give:

$$\mu_g = \frac{S_2 - S_1}{2}\sqrt{\frac{hca^3}{2S_1}} \qquad (10)$$

$$\mu_e = \frac{S_1 + S_2}{2}\sqrt{\frac{hca^3}{2S_1}} \qquad (11)$$

Provided the molecular symmetry is kept the same during the excitation process.

Dependence of the Stokes shift, $\Delta\nu$, on the solvent polarity function, $f(\varepsilon,n)$, according to Eq. 3 gives a slope, S_1, of 1824.0 ($R^2 = 0.89$) and 3115.0 ($R^2 = 0.92$) for 1NA4S and 2NA6S, respectively, while the

dependence of $\Sigma\nu$ on $\phi(\varepsilon,n)$, according to Eq. 4, gives a slope, S_2, of 5577.0 ($R^2 = 0.92$) and 5347.0 ($R^2 = 0.85$) for 1NA4S and 2NA6S, respectively.
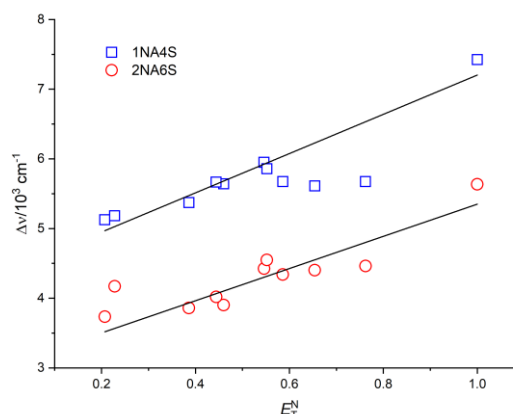

Fig. 5. Dependence of the Stokes shift, $\Delta\nu$, on the solvent polarity parameter, E_T^N.

Accordingly, values of 6.6 D and 3.0 D were obtained for the ground state dipole moments of 1NA4S and 2NA6S, respectively, using Eq. 10, and excited state dipole moments of 12.7 D and 11.1 D were obtained for 1NA4S and 2NA6S, respectively, using Eq. 11.

Reichardt [35, 44] also correlated the spectral data with E_T^N values; which is a dimensionless solvent polarity parameter which developed by Ravi et al [45] according to the following Eq.

$$\Delta\nu = 11{,}307.6\left(\frac{\Delta\mu^2 a_B^3}{\Delta\mu_B^2 a^3}\right)E_T^N + \text{constant} \qquad (12)$$

where a is the Onsager cavity radius of the solute and $\Delta\mu$ is the dipole moment change. a_B and $\Delta\mu_B$ are the corresponding parameters for the betaine dye. Dependence of the Stokes shift versus E_T^N (Eq. 12) gives a slope, S, that can be used in Eq. 13 for the calculation of the dipole moment change ($\Delta\mu$) for 1NA4S and 2NA6S:

$$\Delta\mu = \mu_e - \mu_g = \sqrt{\frac{81\,S}{11{,}307.6\left[\frac{6.2}{a}\right]^3}} \qquad (13)$$

Correlation of the Stokes shift with E_T^N according to Eq. 12 is shown in Fig. 5. In contrast to our previous observation [2, 6-10] that the dependence of $\Delta\nu$ on E_T^N always presented two groups of solvents one for protic and other for aprotic solvents, the current set of compounds show linear dependence for 1NA4S and 2NA6S on E_T^N as shown in Fig. 5.

Dependence of $\Delta\nu$ on E_T^N results in a slope of 2816.0±300.0 ($R^2=0.86$) for 1NA4S and 2309.0±250.0 ($R^2=0.91$) in case of 2NA6S. Incorporation of these values into Eq. 13 results in

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$\Delta\mu$ of 4.3 ± 0.4 D and 4.0 ± 0.4 D for 1NA4S and 2NA6S, respectively.

For precise evaluation of the solvent parameter effect on the photophysical properties of any fluorophore; number of multiparametric relationships were used. The first of which was that introduced by Kamlet-Taft (Eq. (14)) and improved by Catalán (Eq. (15)), and recently by Laurence et al. (Eq. (16)). The equation introduced by Kamlet-Taft [36], has correlated the strength of solvent's acidity, solvent's basicity together with the solvent dipolarity/polarizability (π^*) as follows:

$$A = A_0 + p\pi^* + a\alpha + b\beta \qquad (14)$$

where p, a and b are the susceptibility constants and A_0 is the solvent dependent property in a reference solvent.

Fig. 6 a-c shows the calculated absorption energy, emission energies and Stokes's shift according to Kamlet-Taft's model (Eq. 14) versus their corresponding experimental values. Multilinear regression fitting using Kamlet-Taft model (Eq. 14) shows that solvent's dipolarity/polarizability (π^*) has the lowest effect on the absorption energy while α, and β have about equal contribution for both compounds. On the other hand, solvent's dipolarity/polarizability (π^*) has the highest contribution to the emission energy, n_e, with about 64.0 %, while α has the lowest contribution, and β slightly higher than a. Dependence of the Stokes shift on Kamlet-Taft parameters show that the solvent's dipolarity/polarizability (π^*) has the highest contribution with about 51.0%, followed by the solvent's acidity strength (α) with about 36.0% and only about 13.0 % for the contribution of the solvent's basicity strength (β) in case of 1NA4S. It has been found that the solvent's acidity strength (α) has the highest contribution of about 45.0% to the Stokes shift in case of 2NA6S followed by the solvent's dipolarity/polarizability (π^*) with contribution of about 32.0% and considerable contribution of about 23.0% from the solvent's basicity strength (β).

Catalán [37,38] expanded Kamlet-Taft π^* into two parameters namely; solvent polarizability (SP) and dipolarity (SdP):

$$A = A_0 + sSP + dSdP + aSA + bSB \qquad (15)$$

where SA is the solvent's acidity and SB is the solvent's basicity.

Fig. 7 shows the calculated values according to Catalán's treatment (Eq. 15) of the absorption energy, ν_a, emission energy, ν_e, and Stokes's shift, $\Delta\nu$, versus their experimental values. Insets of the Fig. 7 show the relative contribution of the parameters defined by Catalán.

It can be observed that the sum of the solvent polarizability (SP) and the dipolarity (SdP) parameters (originally Kamlet-Taft

dipolarity/polarizability parameter (π^*)), have higher contribution than that observed from Kamlet-Taft equation for the absorption energy, slightly higher for the emission energy and about equal for the Stokes shift for 1NA4S and much higher for 2NA6S. Such an observation indicates the importance of charge transfer interactions in the ground and the excited states. In addition, solvent's basicity contribution was found to be less important than that designated by Kamlet-Taft equation.

Recently, Laurence et al. [39] have introduced new parameters to describe the dispersion and induction interactions, DI, and the electrostatic interactions, ES, parameters, while α and β parameters have the same definition as have been described by previous models.

$$A = A_0 + diDI + eES + a_1\alpha + b_1\beta \qquad (16)$$

where di, e, a, and b are the corresponding regression coefficients.

Inset of Fig. 8 shows that the contribution of dispersion and induction interactions, DI, and the electrostatic interactions, ES, are dominating factor with the major effect from the former which is consistent with Catalán's model. It has also been found that non-hydrogen interaction (DI and ES) parameters show much higher participation that quoted by Kamlet-Taft model for the absorption energy.

Further inspection to the data given in Fig. 8 shows that the participation of hydrogen bonding interaction parameters contributes considerably to the photophysical properties, Kamlet-Taft treatment show that they are dominating for the absorption energy with about equal contribution for both compounds.

On the other side, their participation to the emission energy and Stokes shift are considerably high but not as high as observed for the absorption energy. In fact, the high contribution of the solvent's basicity observed from Kamlet-Taft treatment is not consistent with the photobasicity characteristics of 1NA4S or 2NA6S

Laurence's treatment has shown that hydrogen bond parameters contribution is less than quoted by Kamlet-Taft treatment but still show that the solvent's basicity competes considerably with the solvent's acidity. Catalán's treatment shows that solvent's acidity contributes much higher than the solvent's basicity to all photophysical properties for both compounds and that the solvent's basicity contribution is minimal. Catalán's treatment also shows that non-hydrogen bonding parameters are dominating with higher contribution from the solvent's polarizability to all photophysical properties for both compounds.
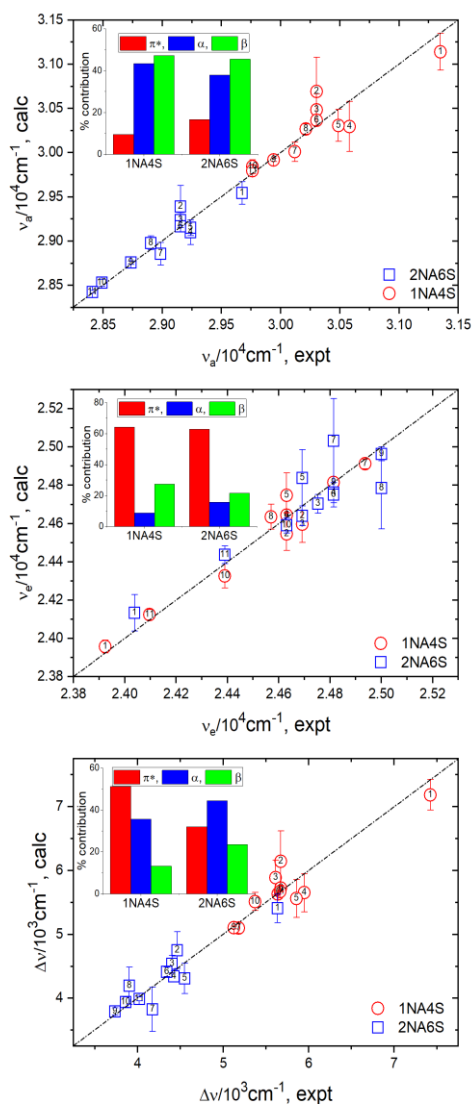
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Fig. 6: Calculated values of the absorption energy, ν_a, emission energy, ν_e, and Stokes shift, $\Delta\nu$ according to Kamlet-Taft Eq. (14) versus their corresponding experimental values, for 1NA4S and 2NA6S

Conclusions

Solvent effect on the photophysical properties of two naphthylamine derivatives has shown that the excited state charge transfer is sensitive to the environment as shown by the spectral shifts in the ground and excited states. Three models have been used to assess the contribution of specific and non-specific interactions on each individual photophysical property.

Conflicts of interest

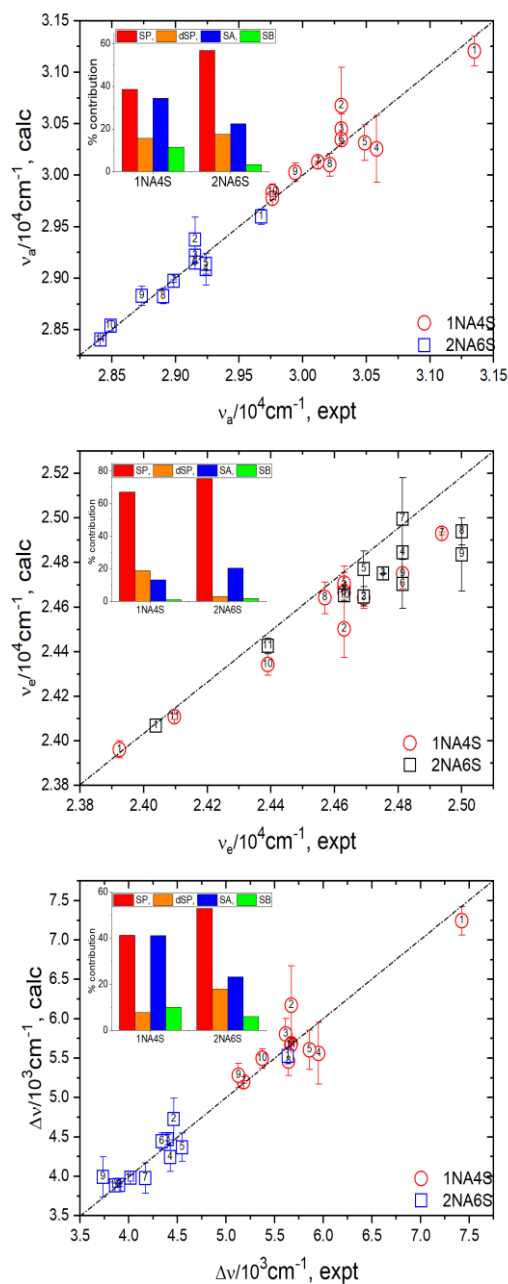"There are no conflicts to declare".

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Fig7: Calculated values according to Catalán Eq. (15) versus experimental values of absorption energy, ꞏa, emission energy, ꞏe, and Stokes shift, ꞏꞏ, for 1NA4S and 2NA6S
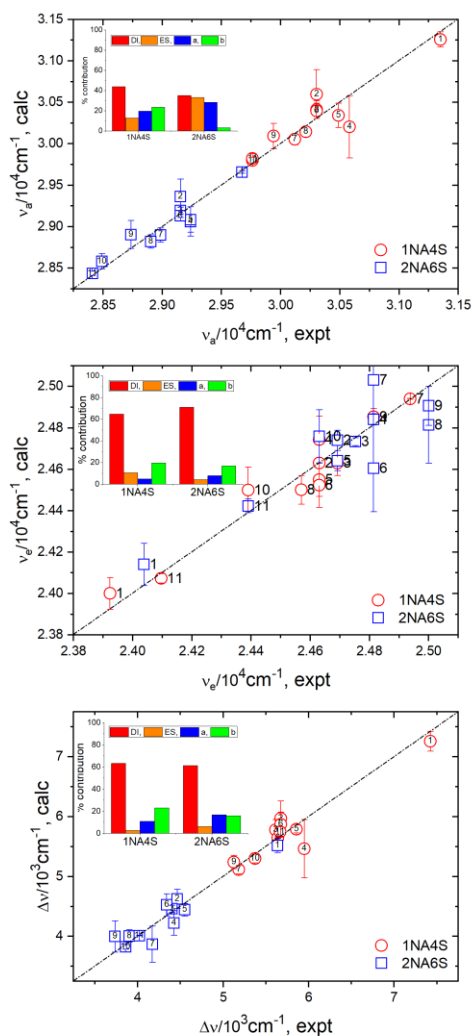
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Fig. 8: Calculated values of the absorption energy, ν_a, emission energy, ν_e, and Stokes shift, $\Delta\nu$, according to Laurence's treatment (Eq. (16) versus their corresponding experimental values for 1NA4S and 2NA6S.

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