Solvatochromic shifts of naphthalene and pyrene excimers

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Abstract

Solvatochromic shifts of pyrene (Py) and naphthalene (Np) excimers were obtained in polar and non-polar solvents. The observed shifts for both excimers are explained by changes in the polarizability between the excimer and the dissociative ground state. The magnitudes of the shifts in the pyrene excimer are larger, indicating that the pyrene excimer is more polarizable than the naphthalene excimer.

1. Introduction

The displacement of the excimer fluorescence band in several solvents — solvatochromic shift — can be well described in terms of the change in the polarizability between the excited and ground states [1].

The shifts in non-polar solvents result from dispersion interactions, whereas in polar solvents the solvent Stark effect must also be considered, the solute transition dipole moment contribution being negligible. This was confirmed for the pyrene excimer, from both solvatochromic shifts [1] and thermochromic shifts [2].

In this paper, solvatochromic shifts of pyrene and naphthalene excimers, in polar and non-polar solvents, are compared. Both excimers display a similar behaviour; the solvatochromic shifts for the naphthalene excimer are smaller than those for the pyrene excimer. This shows that the difference in polarizability between the excimer state and the dissociative ground state is larger for pyrene. This is attributed to differences in both the excimer volumes and the nature of the excimer electronic states.

2. Theory

The solvatochromic shifts of absorption or emission bands result from the different solvation energies of the initial and final electronic states [3, 4].

In polar media, the shift of the emission spectrum ($\Delta E_{ex}$)$_{1-2}$ of a non-polar solute (without considering specific interactions) between two solvents 1 and 2 is the sum of the contributions of three terms: the solvent Stark effect, dispersion interactions and the solute transition dipole moment.

The solvent Stark effect describes the motion of solvent dipoles around the solute molecule [3, 5]

$$\Delta E_{ex} = \frac{-108kT(\alpha_e - \alpha_g)}{R^3} \times \ln^3 \left( \frac{R}{a} \right) \Delta \left[ \frac{(e-n^2)(2e+n^2)}{e(n^2+2)^2} \right]_{1-2}$$

(1)

where $k$ is the Boltzmann constant, $T$ is the absolute temperature, $R$ is the radius of the solvent shell, $a$ is the Onsager cavity radius, $\alpha_e$ and $\alpha_g$ are the solute polarizabilities in the excited and ground states, $\epsilon$ is the solvent dielectric constant and $n$ is the solvent refractive index. (The equations are presented in the simple form used with c.g.s. (e.s.) units, for consistency with most of the papers in the same field. For SI units, the factor $1/(4\pi\epsilon_0)$ should be used.)

Dispersion interactions result from fluctuations in the instantaneous dipole moments of both the solvent and solute molecules [4, 6]

$$\Delta E_{ex} = \frac{C(\alpha_e - \alpha_g)}{a^3} \Delta f(n^2)_{1-2}$$

(2)

where $C$ is the London constant and

$$\Delta f(n^2) = \Delta \left[ \frac{2(n^2-1)}{2n^2+1} \right]$$

(3)
The solute transition dipole moment term accounts for the motion of electric charges during the electronic transition \[\text{(4)}\]

\[
\Delta E_{e_2} = -\frac{M^2}{2a^3} \Delta f(n^2)_{1-2}
\]

where \(M\) is the solute transition dipole moment.

In non-polar solvents, only dispersion interactions and solute transition dipole moment terms contribute to spectral shifts, whereas in polar media the solvent Stark effect must also be considered.

If the solute molecule is polar, there are other contributions to the total spectral shifts. The solute dipole can induce a dipole moment in a non-polar solvent, resulting in a shift given by \[\text{(4)}\]

\[
\Delta E_{e_2} = -\frac{\mu_e^2 - \mu_g^2}{2a^3} \Delta f(n^2)_{1-2}
\]

where \(\mu_e\) and \(\mu_g\) are the solute permanent dipole moments in the excited and ground states respectively.

In polar solvents, the dipole–dipole interaction gives rise to another term \[\text{(4)}\]

\[
\Delta E_{e_2} = -\frac{\mu_e(\mu_e - \mu_g)}{a^3} \Delta [\epsilon_f - f(n^2)]_{1-2}
\]

where

\[
\Delta [\epsilon_f - f(n^2)] = \Delta \left[\frac{2(e-1)}{2e+1} - \frac{2(n^2-1)}{2n^2+1}\right]
\]

The study of solvatochromic shifts can provide information on the nature of the electronic states involved in the transition and allows the evaluation of the dipole moments and/or polarizabilities of the excited electronic states.

3. Experimental details

Naphthalene (Np) (scintillation grade, Nuclear Enterprises) was recrystallized three times from absolute ethanol and dried under vacuum. Pyrene (Py) (99% pure, Koch-Light) was zone refined (100 steps).

Spectroscopic grade acetic anhydride, acetone, acetonitrile, benzene, cyclohexane, dimethyl sulfoxide (DMSO), ethanol, iso-octane, methanol, n-hexane, tetrahydrofuran (THF) and toluene (from Merck), 1,4-dioxane (Panreac) and \(N,N\)-dimethylformamide (Janssen Chimica) were used as received. Methylcyclohexane (BDH, better than 95% pure) and cyclopentane (Fluka, better than 99% pure) were purified by fractional distillation at normal pressure.

Corrected fluorescence spectra of degassed Py and Np solutions were recorded on a Spex Fluor-
rolog 112 spectrofluorometer at room temperature. The excimer band was obtained by subtracting the monomer fluorescence (recorded from dilute solutions, [Np] \(\approx 10^{-3} \) M and [Py] \(\approx 2 \times 10^{-6} \) M) from the full spectrum of solutions of [Np] \(\approx 0.8 \) M and [Py] \(\approx 10^{-2} \) M in the same solvent, after normalizing both spectra to the first peak of the monomer emission.

4. Results and discussion

Both Np and Py excimer emission spectra exhibit red shifts with increasing solvent polarity (Figs. 1(a) and 2(a)). These shifts are small, but can be evaluated accurately from the displacement required to superpose the spectra in various solvents with that obtained in the reference solvent (Figs. 1(b) and 2(b)).

For the Np excimer, the solvatochromic shifts relative to n-hexane are significantly smaller than those obtained for the Py excimer. In polar solvents, \(\Delta E < 1150 \text{ cm}^{-1} \) for Py [1] and \(\Delta E < 650 \text{ cm}^{-1} \) for Np (both values in DMSO), whereas in non-polar solvents, \(\Delta E \approx 970 \text{ cm}^{-1} \) for Py [1] and \(\Delta E \approx 420 \text{ cm}^{-1} \) for Np (both values in benzene).

The excimer shifts in non-polar solvents correlate linearly with \(\Delta f(\kappa^2)_{\text{solv-nhex}} \) (solute dipole-solvent dipole interaction) for polar solvents (Fig. 4) shows no correlation for the Py and Np excimers. This type of interaction is not significant in these systems, indicating that the excimers do not have a permanent dipole moment, contrary to the assumption of Ghosh and Basu [8].

The experimental shifts \((\Delta E)_{\text{exp}} \) in polar solvents were fitted, by a linear least-squares method, to the equation

\[
(\Delta E)_{\text{exp}} = A \Delta \left[ \frac{(e-n^2)(2e+n^2)}{\varepsilon(n^2+2)^2} \right] + B \Delta \left[ \frac{2(n^2-1)}{2n^2+1} \right] \tag{8}
\]

where the first term represents the solvent Stark effect and the second the sum of the contributions of dispersion interactions and the solute transition dipole moment (see eqns. (1)-(4)).

![Fig. 2. (a) Fluorescence spectra of Np excimer in several solvents: (A) n-hexane; (B) methylcyclohexane; (C) 1,4-dioxane; (D) benzene; (E) N,N-dimethylformamide; (F) DMSO. (b) Superposed excimer fluorescence spectra of (a), obtained by normalization of the maximum intensity and wavenumber shifting.](image-url)
The calculated shifts vs. the experimental values, without acetonitrile (a self-associating medium [1, 4]), follow straight lines (r = 0.99 for Np (Fig. 5(a)) and r = 0.97 for Py (Fig. 5(b)), with zero intercept and unit slope (within experimental error). This behaviour indicates that eqn. (8) is adequate to describe the excimer interactions in polar solvents.

The solvent Stark effect coefficients are $A=(1.6 \pm 0.5) \times 10^2$ cm$^{-1}$ [1] and $A=(0.7 \pm 0.1) \times 10^2$ cm$^{-1}$ for Py and Np excimers respectively, showing the difference in magnitude of the excimer shifts.

The parallel behaviour of Py and Np excimers in both polar and non-polar media proves the similarity of the solute-solvent interactions. The linear correlations observed show that the contributions responsible for the excimer shifts are the dispersion interactions, solute transition dipole moment term (if important) and, in polar media, also the solvent Stark effect.

The contribution due to the transition dipole moment term can be estimated from the radiative rate constant $k_F$ [9]

$$k_F=1.162 \times 10^{-5} \pi^2 \langle \nu^{-3} \rangle_A^{-1} |M|^2$$  \hspace{1cm} (9)

where

$$\langle \nu^{-3} \rangle_A^{-1} = \int [F(\nu) d\nu] / \int [F(\nu) d\nu / \nu^3]$$  \hspace{1cm} (10)

where $F(\nu) d\nu$ is the molecular fluorescence intensity at frequency $\nu$.

Using the experimental excimer emission spectra and the published values of $k_F$ (1.05 $\times$ 10$^7$ s$^{-1}$ in n-hexane, 1.16 $\times$ 10$^7$ s$^{-1}$ in cyclohexane, 1.0 $\times$ 10$^7$ s$^{-1}$ in acetone and 1.07 $\times$ 10$^7$ s$^{-1}$ in ethanol [10, 11] for the Py excimer, and 0.9 $\times$ 10$^6$ s$^{-1}$ in toluene [12] for the Np excimer), the transition excimer dipole moments of $M=1.25 \pm 0.02$ D and $M=0.23$ D were calculated for Py and Np respectively.

The excimer cavity radius $a$ was estimated as [13]

$$a=\left(\frac{3}{2\pi N_A} V_\Lambda\right)^{1/3}$$  \hspace{1cm} (11)

where $V_\Lambda$ is the molar volume of the monomer. The Le Bas additive correlation [14] was used to
evaluate the Py and Np molar volumes. The excimer cavity radii determined are 5.5 Å for Py and 4.9 Å for Np.

These values lead to $|M|^2/2a^3 = 4.7 \times 10^{-15} \text{erg}$ (approximately 24 cm$^{-1}$) for the Py excimer and $|M|^2/2a^3 = 2.2 \times 10^{-16} \text{erg}$ (approximately 1 cm$^{-1}$) for the Np excimer, which makes the contribution of the transition dipole moment term to the total shifts negligible. Therefore the shifts in the Py and Np excimer emissions are caused by changes in the polarizability between the excited and ground states.

The notable difference in the magnitude of the shifts for the two excimers indicates distinct values of the polarizability variation $\Delta \alpha = \alpha_e - \alpha_g$. However, the large uncertainty in the estimation of the London constant $C$ and the cavity radius $a$ make any values of $\Delta \alpha$ calculated from these correlations unreliable [6]. Nevertheless, by considering ratios of the Py and Np coefficients for dispersion interactions and the solvent Stark effect, qualitative trends for $\alpha_e - \alpha_g$ can be obtained.

Assuming equal values for the London constant in both excimers, we obtain from dispersion interactions (see eqn. (2))

$$\left(\frac{\alpha_{Np \cdots Np^*}}{\alpha_{Py \cdots Py^*}}\right) \frac{\Delta \alpha_{Py \cdots Py^*}}{\Delta \alpha_{Np \cdots Np^*}} = 2.1 \pm 0.6$$  \hspace{1cm} (12)

where Np$\cdots$Np$^*$ and Py$\cdots$Py$^*$ are the Np and Py excimers respectively. This allows the calculation of a polarizability difference ratio

$$\frac{\Delta \alpha_{Py \cdots Py^*}}{\Delta \alpha_{Np \cdots Np^*}} = 3.0 \pm 0.9$$  \hspace{1cm} (13)

Considering that $R \approx 3a$ [5], a similar relation can be obtained from the solvent Stark effect, since the experimental measurements were made at the same temperature (see eqn. (1))

$$\frac{\Delta \alpha_{Py \cdots Py^*}}{\Delta \alpha_{Np \cdots Np^*}} = 3 \pm 1$$  \hspace{1cm} (14)

The similar polarizability difference ratios from eqns. (13) and (14) show that the assumption of equal $C$ values for both excimers is acceptable, since the equation for the solvent Stark effect (eqn. (1)) does not contain this parameter.

The $\alpha_g$ value is assumed to be twice the monomer ground state polarizability. (We were unable to find in the literature the ground state polarizability of Py. As $\alpha_g$ values for compounds with the same number of aromatic rings are similar (e.g. anthracene and phenanthrene [15, 16]; 3,4-benzopyrene and 1,2:5,6-dibenzanthracene [16]), we used the $\alpha_g$ value of tetracene [15] for Py.)
\[(\alpha_e)_{\text{Py}+\text{Py}} = 74 \text{ Å}^3 [15],\]
\[(\alpha_e)_{\text{Np}+\text{Np}} = 34 \text{ Å}^3 [17].\]

From eqns. (13), (14) and (15) we obtain
\[(\alpha_e)_{\text{Py}...\text{Py}*} = 3(\alpha_e)_{\text{Np}...\text{Np}*} - 28 \text{ Å}^3 \]

According to this relation, \((\alpha_e)_{\text{Py}...\text{Py}*} \gg (\alpha_e)_{\text{Np}...\text{Np}*},\) which means that the Py excimer is much more polarizable than the Np excimer. This results from differences in both the excimer volumes and the nature of the electronic states.

The nature of excimer states has been described as a configurational mixing between exciton resonance (ER) and charge resonance (CR) states [11, 18, 19]. In this model, each ER state \(1^{\text{E}}(\text{E})\) is mixed with the CR state \(1^{\text{R}}(\text{R})\) of the same symmetry, yielding a pair of singlet excimer states \(1^{1:\text{E}+\text{R}},\) of which \(1^{1:\text{E}-\text{R}}\) has the lowest energy [11]. In catacondensed hydrocarbons, \(1^{1\text{L}}_{\text{o}}\) and \(1^{1\text{L}}_{\text{a}}\) (Platt's notation) correspond to \(S_1\) and/or \(S_2\) states, whereas \(1^{1\text{B}}_{\text{a}}\) and \(1^{1\text{B}}_{\text{b}}\) are higher energy states [11, 19]. The most probable Np lowest excimer state seems to be \((1^{1\text{L}}_{\text{o}}E-1^{1\text{R}}),\) the lower ER state (symmetry: \(1^{1\text{B}}_{\text{a}}\)) originating from the molecular \(1^{1\text{L}}_{\text{o}}(S_2)\) state, stabilized by configurational mixing with the corresponding CR state [11, 19]. The Py lowest excimer state probably results from configurational mixing of the ER \((1^{1\text{B}}_{\text{a}}),\) ER \((1^{1\text{L}}_{\text{a}})\) and CR states of \(1^{1\text{B}}_{\text{b}}\) symmetry, the ER \((1^{1\text{B}}_{\text{a}})\) state being dominant [11, 18]. This predominant state, originating from a higher molecular \((1^{1\text{B}}_{\text{b}})\) state, is presumably more polarizable than the lowest Np excimer state, deriving from the molecular \(1^{1\text{L}}_{\text{a}}\) state. Nevertheless, the main contribution to the difference between the Py and Np excimer polarizabilities results from the larger volume of the Py excimer, \(V_{\text{Py}...\text{Py}*} = 1.5V_{\text{Np}...\text{Np}*}.\)

5. Conclusions

Solvatochromic shifts of Py and Np excimers in polar and non-polar solvents show that the excimers are non-polar. Spectral shifts result from the differences in polarizability between the excimer and the dissociative ground state.

The calculation of the polarizabilities in the excited states from the solvatochromic shifts in polar and non-polar media indicates that the Py excimer is more polarizable than the Np excimer. This is attributed to differences in both the excimer volumes and the nature of the lowest energy excimer states.

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