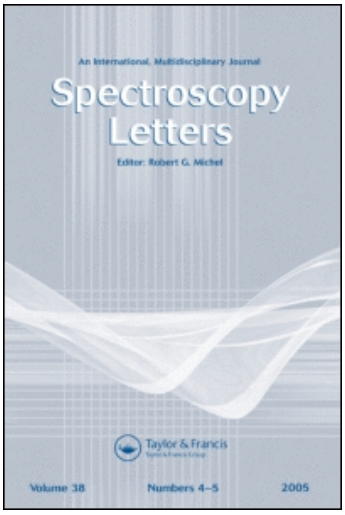

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Correspondence of Fluorescing States of Naphthols and Naphtholate Anions and its Effect on the Calculation of pK_a^* from Spectral Shifts

Stephen G. Schulman[a]
[a] College of Pharmacy University of Florida, Gainesville, Florida

To cite this Article Schulman, Stephen G.(1973) 'Correspondence of Fluorescing States of Naphthols and Naphtholate Anions and its Effect on the Calculation of pK_a^* from Spectral Shifts', Spectroscopy Letters, 6: 3, 197 — 202
To link to this Article: DOI: 10.1080/00387017308065448
URL: http://dx.doi.org/10.1080/00387017308065448

SPECTROSCOPY LETTERS, 6(3), 197-202 (1973)

Correspondence of Fluorescing States of Naphthols and Naphtholate Anions and its Effect on the Calculation of pK_a^* from Spectral Shifts

by

Stephen G. Schulman

College of Pharmacy
University of Florida
Gainesville, Florida 32601

The validity of dissociation constants of electronically excited acids and bases, calculated from spectral shifts[1, 2] accompanying protolytic dissociation, especially where shifts of fluorescence spectra are employed, is dependent, among other factors, upon fluorescence orginating from excited states of the same electronic configuration in both acid and conjugate base.[3] In some of the molecules whose excited state acid-base properties have been most extensively studied, notably some derivatives of naphthalene, energy level reversals have been shown to accompany dissociation in the lowest excited singlet state in aqueous solutions.[4] The spectroscopic properties and excited state dissociation phenomena of the naphthols have been studied extensively from several points of view.[5-9] While the calculation of the excited state dissociation properties of β-naphthol, in which fluorescence occurs from the ^1L_b state in both anion and neutral molecule, presents no particular problem with regard to correspondence of the lowest excited singlet states of conjugate acid and base, it appeared that in α-naphthol, by analogy with α-naphthylamine[4], fluorescence might occur from the ^1L_a state in the conjugate base and from the ^1L_b state in the conjugate acid. Thus it seemed that a careful consideration of the states from which the fluorescences of the conjugate species derived from α-naphthol in fluid aqueous solutions orginated, would be useful.

The lowest excited singlet state of naphthalene is derived from the longitudinally polarized $^1L_b \leftarrow {}^1A$ transition and fluorescence is thought to arise from the ^1L_b state in naphthalene.[8] Substituents at β-positions of the naphthalene ring have the greatest perturbing influence on the ^1L_b state while those in α-positions of the naphthalene ring have the greatest perturbing influence on the ^1L_a state.[10] The latter clearly lies above the ^1L_b state in the absorption spectrum of naphthalene in which both excited states are thermally excited with respect to solvent cage configuration. In the thermally equilibrated, electronically excited naphthalene molecule the ^1L_a state undoubtedly lies above the ^1L_b state but its actual position is unknown because fluorescence occurs only from the ^1L_b state.

In β-naphthol and the β-naphtholate anion, intramolecular charge transfer from the hydroxyl group and its conjugate anion lower the frequency of the $^1L_b \leftarrow {}^1A$ transition to a greater extent than that of the $^1L_a \leftarrow {}^1A$ transition (Table 1). Thus the ^1L_b states of β-naphthol and its anion lie

Table 1

Absorption ($\bar{\nu}_{^1L_a}$ and $\bar{\nu}_{^1L_a}$) and corrected fluorescence ($\bar{\nu}_f$) maxima of α- and β-naphthol in water. Spectral maxima are reported in $cm^{-1} \times 10^{-4}$.

	Neutral Molecule			Anion		
	$\bar{\nu}_{^1L_a}$	$\bar{\nu}_{^1L_b}$	$\bar{\nu}_f$	$\bar{\nu}_{^1L_a}$	$\bar{\nu}_{^1L_b}$	$\bar{\nu}_f$
α-naphthol	3.47	3.12	2.65	3.01	-*	2.19
β-naphthol	3.68	3.07	2.85	3.57	2.90	2.38

*The ^1L_b band of the 1-naphtholate anion is buried under the more intense ^1L_a band.

even farther below the ^1L_a states of these species than the ^1L_b state of naphthalene lies below its ^1L_a state. Fluorescence in β-naphthol and the β-naphtholate anion must therefore arise from the ^1L_b states. In α-naphthol and its anion, however, the direction of charge transfer from the hydroxyl group is parallel to the $^1L_a \leftarrow {}^1A$ transition moment and the ^1L_a state is lowered in energy by a greater amount than the ^1L_b state. Thus the absorption spectrum of α-naphthol (Table 1) shows the ^1L_a band to lie some 1400-2100 cm^{-1} to lower frequencies than in naphthalene or β-naphthol while the ^1L_b band of α-naphthol is lower by only about 500 cm^{-1}. In the α-naphtholate anion, charge transfer from the oxygen atom to the ring is even more facilitated by the formal negative charge on the oxygen atom which is electron repelling. Thus the ^1L_a band of the α-naphtholate anion lies some 5600-6000 cm^{-1} to the red of the ^1L_a band of naphthalene and the β-naphtholate anion. The position of the ^1L_b band in the absorption spectrum of the α-naphtholate anion is unknown because it is eclipsed by the more intense ^1L_a band. Presumably the position of the ^1L_b band of α-naphtholate is not very different from that in α-naphthol and there is a good chance that the ^1L_a state lies lower than the ^1L_b state. In water, fluorescence from the α-naphtholate anion occurs at lower frequency than that of the β-naphtholate anion. Clearly, this is possible only if the thermally equilibrated ^1L_a state of the α-anion lies lower than the ^1L_b state.

Suzuki and Baba[7] have studied the polarized fluorescence excitation spectra of α-naphthol in hydrocarbon glasses containing hydrogen bond acceptors of varying strength (ether and triethylamine). These studies revealed that at 77°K, in ether doped hydrocarbon glasses, fluorescence arises from the ^1L_b state but in triethylamine doped hydrocarbon glasses, fluorescence originates from the ^1L_a state. However, triethylamine is a slightly stronger base than α-naphtholate and the low frequency of emission reported by these

authors[7] for α-naphthol in the presence of triethylamine is much like that of β-naphtholate in the same type of solvent at room temperature.[11] It is likely that the ^1L_a emission in triethylamine doped hydrocarbon glass, studied by Suzuki and Baba, really corresponds to the fluorescence of the α-naphtholate anion although the fluorescence of α-naphthol in weakly or non-activating solvents must certainly arise from the ^1L_b state. In fluid water, however, the fluorescence of α-naphthol lies 2000 cm^{-1} lower in frequency than that of β-naphthol, indicating that in the activating solvent, relaxation in the excited state has definitely carried the ^1L_a state of α-naphthol below the ^1L_b state. The influence of the activating solvent therefore represents an auxiliary substituent effect on the electronic spectra.

This experiment shows that the assignments of fluorescence spectra to their states or origin by polarized emission measurements are of only limited value when the species of interest are dispersed in fluid, polar or hydrogen-bonding media. Because rotational freedom in fluid media results in essentially complete depolarization of fluorescence excited with polarized light, spectral assignments in fluid media are best studied by relative substituent effects on the spectra of the parent hydrocarbons of the molecules in question.

The dissociation equilibria of α-naphthol and β-naphthol in their lowest excited singlet states are thus shown to occur in the ^1L_a and ^1L_b states respectively. The constants of these equilibria have been determined by kinetic methods derived from fluorometric titrimetry coupled with fluorescence lifetime measurements and were found to be <1.8[9] and 2.9[9], respectively, for the α- and β-isomers. The reason that an upper limit is given for the pK_a^* of the α-isomer is that the lifetime of the ^1L_a state of the neutral α-isomer, from which the rate constant for dissociation is derived, was too short to measure (<1 nanosec.) with the apparatus employed. Calculation of the pK_a^* values of the α- and β-isomers employing the Förster cycle[1] and the averages of the low frequency absorption maxima and fluorescence maxima of the conjugate

acid and base species of each isomer yielded pK_a^* = 2.1 for α-naphthol[9] and pK_a^* = 2.9 for β-naphthol[9], in good agreement with the kinetically determined values, at least for the β-isomer. However, the absorption maximum employed in the averaging process for the neutral α-isomer corresponds to the 0-0 band of the ^1L_b transition. Thus the calculation is at least conceptually in error and the agreement between the kinetically and spectroscopically determined values of pK_a^* for α-naphthol appears to be fortuitous. Employing the averaging technique in the Förster cycle using the ^1L_a maxima and fluorescence maxima of Table 1 and the ground state pK_a of 9.2 a pK_a^* of -0.4 is obtained for α-naphthol. If the ^1L_a absorption maxima or the fluorescence maxima are employed separately in the Förster cycle the same value, -0.4, is obtained in each case for the pK_a^* of α-naphthol, a result that indicates that solvent relaxation and vibrational effects in ground and excited states are of equal magnitude in acid and conjugate base.[12, 13]

In β-naphthol, calculation of pK_a^* by employing the pK_a of 9.5 and the shift of the ^1L_b absorption maximum, upon dissociation, yields pK_a^* = 5.9 while if the fluorescence shift alone is employed a pK_a^* of -0.4 is obtained. Both values are in poor agreement with the kinetically determined value. The difference in frequency between the fluorescence maxima of β-naphthol and its anion is almost identical in hydrocarbon solvents[11] and in water. This indicates that the discrepancy between the pK_a^* values obtained from the absorption shift and the emission shift is not due to unequal solvent relaxation energies of the neutral molecule and anion in the excited state and must therefore be the result of inequalities in the vibrational make-ups of the absorption and fluorescence bands of neutral molecule and anion.[12, 13] The effect upon the calculation of pK_a^* of differences in vibrational composition between spectral bands are often minimized by averaging absorption and fluorescence spectra.[3, 6] Thus calculation of pK_a^* of β-naphthol from the

Förster cycle using the spectral averaging technique yields pK_a^* = 3.2 in good agreement with the kinetically determined pK_a^*.

References

1. T. Förster, Z. Elektrochem. 54, 42 (1950).
2. G. Jackson and G. Porter, Proc. Roy Soc. A260 13, (1961).
3. H. H. Jaffé and H. L. Jones, J. Org. Chem. 30, 964 (1965).
4. N. Mataga, Bull. Chem. Soc. Japan 36, 654 (1963).
5. D. M. Hercules and L. B. Rogers, Spectrochim Acta 14, 393 (1959).
6. A. Weller, Z. Elektrochem. 56, 662 (1952).
7. S. Suzuki and H. Baba, Bull. Chem. Soc. Japan. 40, 2199 (1967).
8. J. R. Platt, J. Chem Phys. 17, 484 (1949).
9. J. L. Rosenberg and I. Brinn, J. Phys. Chem. 76, 3558 (1972).
10. A. E. Lutskii and L. A. Antropova, Zh. Fiz. Khim. 39, 113 (1965).
11. N. Mataga and Y. Kaifu, Mol-Phys. 7, 137 (1963).
12. S. G. Schulman, P. T. Tidwell, J. J. Cetorelli and J. D. Winefordner, J. Amer. Chem. Soc. 93, 3179 (1971).
13. P. J. Kovi and S. G. Schulman, Anal. Chem. Acta, in press.

Received January 15, 1973

Accepted January 31, 1973