

Excited-state dipole moments from absorption and fluorescence solvatochromic shifts – a better approach[†]

NARASIMHA H AYACHIT

Department of Physics, KLE Society's Engineering College, Udyamabag, Belgaum 590 008, India

MS received 15 May 1989

Abstract. Suppan (1983 *Chemical Physics Letters* **94** 270) has proposed an equation to estimate the excited state electric dipole moment from absorption and fluorescence solvatochromic shifts and applied it to the first excited state $L(b)$ of aniline. A better approach to this problem is proposed here, which avoids the assumption in respect of μ_e making an angle with $\Delta\mu_{eg} = \mu_e - \mu_g$; μ_g being ground state electric dipole moment. This approach is expected to give a better estimation of the electric dipole moment of a molecule when it is electronically excited. On testing this approach for aniline in its first excited state μ_e turns out to be 5.31 D.

Keywords. Solvatochromic shifts; excited-state electric dipole moment; aniline.

1. Introduction

The seemingly complex equation for solvatochromic shifts in absorption and fluorescence spectra of a molecule is being used in different simplified forms to estimate the electric dipole moment (μ_e) in an excited state, and finally, to determine the electronic structure of the molecule when it is electronically excited (Lippert 1939; Bilot and Kawaski 1962; Liptay 1965; Suppan 1968, 1983; Keutek 1978; Ayachit *et al* 1986). In this direction, Suppan's (1983) method consists of solvatochromic shifts from the two types of spectra, in two solvents with nearly the same refractive indices but with different static dielectric constants. This method rids itself of the cavity radius (a_0) and function of dielectric constants (D_s) as well as the refractive indices (n_s), of solvents used in the experimental study. Along with some assumptions, it has been applied to the first excited state $L(b)$ of aniline. In this paper, the assumptions which are concerned with the estimation of electric dipole moment in an excited state are questioned and a better approach to the problem is suggested. The approach suggested is applied to the first excited state $L(b)$ of aniline.

[†] In this paper, symbols used are as in Suppan (1983); equation and figure numbers with primes refer to this work while those without are cited from Suppan (1983).

2. Method and discussion

Figure 1 and equation (4) in Suppan (1983) which becomes (1') in this discussion,

$$\frac{(\Delta E_{g-e})_{1-2}}{(\Delta E_{e-g})_{1-2}} = \frac{\mu_g \Delta \mu_{g-e} \cos \zeta \cdot \Delta f(D)_{1-2} a_g^{-3}}{\mu_e \Delta \mu_{e-g} \cos \varphi \cdot \Delta f(D)_{1-2} a_e^{-3}}, \tag{1'}$$

are not compatible. It is not so in respect of the expansion of the term $\mu_g \cdot \Delta \mu_{ge}$ as $\mu_g \Delta \mu_{ge} \cos \zeta$ and $\mu_e \cdot \Delta \mu_{eg}$ as $\mu_e \Delta \mu_{eg} \cos \varphi$ where ζ and φ should now define difference in the directions of μ_g and μ_e respectively with $\Delta \mu_{eg}$. This is shown in figure 1. Proceeding with (5) in Suppan (1983) (which becomes (2') in this paper) obtained from (4) therein as applied to the excited state (L_b) of aniline, it should be clear that the equations are consistent with the discussions, while not with figure 1. Figure 1, therefore, becomes figure 1' by exchanging the positions of ζ and φ .

$$(\Delta E_a / \Delta E_f) = -(\mu_g \cos \zeta) / (\mu_e \cos \varphi). \tag{2'}$$

Now, following Suppan (1983) as to the application of (2'), it is tested for the first singlet excited state of aniline in which he takes $\zeta = 30^\circ$ while assuming φ to be 180° . This assumption, when $\zeta = 38^\circ$, that μ_e lies along $\Delta \mu_{ge}$, while μ_g does not, is not correct. Of course, φ could be nearly 180° in which case its cosine function will approximately be the same as when it is 180° , i.e. it will be -1 .

In view of this, a better approach is suggested; it gives a method to determine φ if ζ is known. It not only rids itself of Suppan's assumption as to φ , but also would give a relatively better estimation of μ_e . Referring to figure 1', two angles z and Φ stand out in relation to ζ and φ respectively as follows:

$$\begin{aligned} z &= 180^\circ - \zeta, \\ \Phi &= 180^\circ - \varphi. \end{aligned} \tag{3'}$$

Invoking the sine rule for triangles, figure 1' gives us,

$$(\sin \Phi / \sin z) = (\mu_g / \mu_e). \tag{4'}$$

Combining (3') and (4') with (2') we get

$$(\Delta E_a / \Delta E_f) = -\tan(180 - \varphi) / \tan(180 - \zeta).$$

Therefore,

$$\varphi = 180 - \tan^{-1} \{ -(\Delta E_a / \Delta E_f) \tan(180 - \zeta) \}. \tag{5'}$$

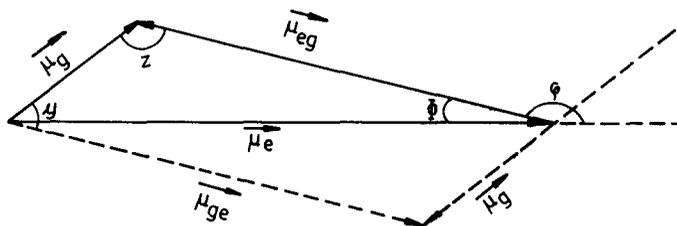


Figure 1'. Definition of angles between the ground state (μ_g) and excited state (μ_e) dipole moment vectors.

Substituting this φ in (2'), one can estimate μ_e with the pre-knowledge of μ_g and ζ . By taking $\zeta = 38^\circ$ and $\Delta E_a/\Delta E_f = 900/3800$ for the singlet excited state of aniline, φ turns out to be 169.5° which differs by about 10° with respect to the φ of Suppan (1983). With this φ , μ_e will be, from (2')

$$\mu_e = -1.57(\cos 38/\cos 169.5)(3800/900)D = 5.31 D$$

where $1.57 D$ is μ_g , the ground state dipole moment of aniline. Apparently this value of μ_e does not differ much from that of Suppan (1983) because of the fact that the cosine function would not change much around 180° .

According to Suppan (1983), ζ and φ can generally be estimated from the geometry of the molecule but in the present case only ζ need be known, which upon substitution into (5') gives φ . Further, if ζ and φ can be pre-known along with μ_g , one can estimate μ_e using (3') and (4') alone. With this it is apparent that the step rids the problem of measuring the solvatochromic shifts to estimate μ_e . In view of this, Suppan's assertion may be questioned.

3. Conclusions

In conclusion, it has been shown that, the common assumption about the inclination of μ_e with $\Delta\mu_{eg}$ as 180° is not reasonable and becomes redundant as it can be fairly determined by (5') given μ_g and ζ .

Acknowledgement

I thank Prof K Suryanarayana Rao, Drs M A Shashidhar, D K Deshpande of Department of Physics, Karnataka University, Dharwad (India), and Principal G G Babladi and other authorities of K.L.E. Society's Engineering College, Belgaum (India) for their encouragement and co-operation. I also wish to thank my colleague Dr J R Tonannavar for useful discussions.

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