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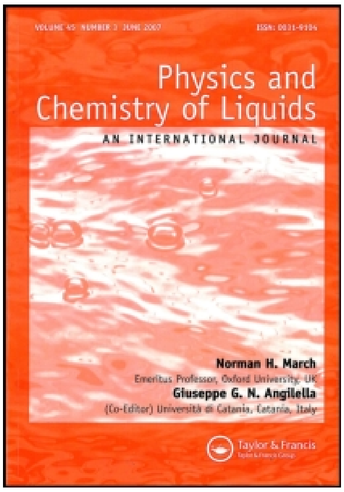

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Excited state polarizabilities from solvatochromic shifts

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Excited state polarizabilities from solvatochromic shifts

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A new method is proposed to estimate the polarizability (α_e) of a molecule in an excited state using solvatochromic shift measurements and McRae's equation. In the earlier methods the contribution due to polarizability was not considered. In view of this, the proposed method is also expected to give a better estimation of excited state electric dipole moment (μ_e) and the (θ) angle between excited and ground state electric dipole moments, μ_e and μ_g apart from giving values of polarizability of the molecules in the excited state. This method has been applied in the case of the La band of *p*-nitro aniline and the results for all the parameters are found to be satisfactory and of right order in comparison with that reported in literature.

Keywords: Electric dipole moment; Polarizability; Electronically excited state and ground state; Solvetochromic shifts; Molecular radius; Solvent dielectric medium

1. Introduction

The determination of electric dipole moment of a molecule and its polarizability in an electronically excited state is an important study considering their relation to the molecular structure, intermolecular forces, molecular vibrations etc. Further these studies make it possible to understand the photochemical reactions as well as electronic transitions in question. McRae's equation [1] has been exploited by several researchers [2–17] to estimate the electric dipole moment of a molecule in an excited electric state (μ_e) using measurements of solvetochromic shifts. Different approaches have been adopted to have a good estimation of excited state electric dipole moment of a molecule (μ_e), which mainly concentrates on the simplification of McRae's equation. One of the restrictions commonly imposed for the simplification of the equation is to choose only those solvents, which have their refractive indices very close (n). A method is also available in which the choice of the solvents is not restricted [13]. From these methods one cannot estimate excited electronic state polarizability (α_e) as in those methods it is assumed, in general, that the contribution of the change in polarizability

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of a molecule from ground state to excited state to solvatochromic shifts, is negligible. Abe [18] has given an equation to estimate excited state polarizability of a molecule. This equation contains a term which is complicated and is a function of ionization potentials and molar volumes of solvent and solute molecules apart from their dielectric constants (D), refractive indices (n) of solvents, position of a band of maximum intensity (ν_{max}) in the UV region and the ground state polarizability (α_o). From this method, one can estimate α_e fairly satisfactorily but is quite a complicated method.

In this article, a simple method for the estimation of excited state electric polarizability (α_e) of a molecule is given, in which the contribution due to the change of polarizability of a molecule from the ground state (α_o) to the excited state (α_e) to solvatochromic shift is taken in to account in McRae's equation [1]. By accounting to this contribution, this method is also expected to give a better estimation of the excited state electric dipole moments (μ_e) and the angle (θ) between the ground and excited state dipole moments. This method has been applied in the case of La band of p-nitro aniline. The ground state dipole moment (μ_g), the ground state polarizability (α_o) and molecular radius (a_0) are taken from literature [18]. The values obtained for μ_e, θ and α_e are found to be satisfactory and of right order.

2. Method

In the light of McRae's theory of the solvent effect on the electronic spectra [1], the frequency of maximum solute absorption in a solvent ν_s can be expressed as

$$\nu_s = \nu_0 + (A + B + C)f(n_s) + E[f(D_s) - f(n_s)] + F[f(D_s) - f(n_s)]^2 \tag{1}$$

where ν_0 is the corresponding vapor phase frequency of ν_s, $f(n_s) = (n_s^2 - 1)/(2n_s^2 + 1)$ is a function of solvent refractive index (n_s), $f(D_s) = (D_s - 1)/(2D_s + 1)$ is a function of solvent dielectric medium (D_s), $(A + B)$ is a measure of dispersive effect, $C = (\mu_e^2 - \mu_g^2)/hca_0^3$ and h and c are Plank's constant and velocity of light respectively. The last term in equation (1), so far neglected in previous studies by others has now been taken into account.

Equation (1) can be written as

$$\nu_s = \nu_0 + (A + B)f(n_s) + (C - E)f(n_s) + F[f(n_s)]^2 + [E - 2Ff(n)]f(D) + F[f(D_s)]^2$$

if ν_1 and ν_2 are the positions of maxima of a band of solute molecule in solvents 1 and 2, of nearly the same refractive indices i.e. nearly same $f(n_s)$, but of different dielectric constants D_1 and D_2, then

$$\nu_1 - \nu_2 = [E - 2Ff(n)][f(D_1) - f(D_2)] + F\left\{[f(D_1)]^2 - [f(D_2)]^2\right\}$$

i.e.

$$\frac{\nu_1 - \nu_2}{[f(D_1) - f(D_2)]} = [E - 2Ff(n)] + F[f(D_1) + f(D_2)] \tag{2}$$

Here, it is assumed that the contribution of $(A + B)$ is very small. As the difference is involved the contribution becomes still small and hence negligible, more over earlier works have shown that the contribution of the dispersion effect to the frequency shift is nearly the same for different kinds of solvents.

If one chooses a set of solvents of nearly same refractive indices and of a fairly wide range of dielectric constants to record the electronic spectra of a solute molecule in solution, then the term $[E-2Ff(n)]$ can be taken as constant for a given set of solvents, under the restriction mentioned above. This, equation (2) can be put in the form of an equation of a straight line

$$\left.\begin{aligned} Y &= mX + C \\ \text{with } X &= [f(D_1) - f(D_2)] \\ Y &= \frac{\nu_1 - \nu_2}{[f(D_1) - f(D_2)]} \\ m = F &= \mu_g^2 \frac{(ag - ae)}{hca_0^6} \\ C &= [E - 2Ff(n)] \end{aligned}\right| \tag{3}$$

For every two solvents out of the set of the solvents chosen of nearly the same refractive indices, one can obtain the values of X and Y. By plotting a graph of Y *versus* X, it is possible to obtain the slope m i.e., F and hence α_e can be determined using the pre-determined values of α_g, μ_g and a_0, using the above formula, namely,

$$\alpha_e = \left[\alpha_g - \frac{Fhca_0^6}{\mu_g^2}\right]. \tag{4}$$

Using the method given earlier [5] and by noting the position of the band in a series of non-polar solvents one can calculate μ_e. From this value of μ_e and using the value of intercept C obtained from the method given above the angle between μ_e and μ_g can be calculated as follows,

$$E = C + 2Ff(n) = \frac{\mu_g \cdot \Delta\mu_{ge}}{hca_0^3} = \frac{|\mu_g|^2 - |\mu_e||\mu_g|\cos\theta}{hca_0^3}$$

i.e.,

$$\theta = \cos^{-1}\left\{\frac{|\mu_g|^2 - hca_0^3[C + 2Ff(n)]}{|\mu_e||\mu_g|}\right\}. \tag{5}$$

Here, $f(n)$ is obtained by taking mean of all the $f(n)$'s, which of course would be very close in value.

3. Application

This method has been applied in the case of L_a band of *p*-nitro aniline by using the literature values for $\nu_{\max}$ in different solvents [18]. The values α_g and μ_g are also taken from the same literature [18] which are respectively 157.00–25 cm^3 (obtained for a deformation polarization for nitrobenzene) and 6.13D (obtained through the method of combination of bond refractions. Here we use the value of a_0 as obtained by the method of atomic increments. The plot of Y *versus* X obtained in the case of L_a band of *p*-nitro aniline is used for the calculation. In this work, cyclohexane is taken as reference solvent i.e., it has been treated as solvent 1 and all other solvents as solvent 2 and accordingly

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values of X and Y have been determined. The care should be taken that only one non-polar solvent is chosen in a given set of solvents. If two non-polar solvents are chosen then the assumption in applying equation (2) to such set of solvents will not be appropriate as, for a non-polar solvent n^2 is approximately equal to D_s. For two solvents of nearly same refractive index their $f(D)$ values will almost remain the same, which is wrong as per the assumption made in implementing equation (2). Further, even if one chooses that way then the value of Y will tend to be very high as the denominator almost tends to zero for a set of non-polar solvents.

In the present work the nature of the points indicates that the data fits for a straight line as expected. The values of μ_e, θ and α_e obtained respectively in the present work are 8.26D, 42° and $658.7E{-}25\,cm^3$. The value of α_e obtained is more than that of α_g, but is quite less than the value of α_e obtained by using Abe's method [18]. The large variation in the excited state dipole moment in comparison with its ground state dipole moment tends to infer that the absorption band is a charge transfer one and probably polarized along the twofold symmetry axis as in the case of aniline. It may also be inferred that the transition involved is of a $\pi^*\pi$ type as the dipole moment increases as in the excited state in comparison with respect to the ground state.

This method is better than Abe's method for the reasons mentioned in Introduction. Apart from this, the present method being graphical, it allows us to eliminate the points which are much away from a straight line, which might have occurred with much deviation because of some interactions which are not accounted for in McRae's equation like hydrogen bonding, anomalous behavior of solvents, formation of dimmers etc. In case of Abe's method since linear fit is carried out, such elimination of points is not possible unless one adopts rigorous statistical approach. This method proposed here thus neglects the effect of specific interactions such as H-bonding. The method of obtaining a_0 is a much-discussed matter. Hence, if this method is also freed of use of a_0 as has been done in case of those methods which neglect polarizability, the values estimated can still be accurate.

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