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Determination of Excited State Electric Dipole Moments and Polarizabilities of positional Isomeric Nitroaniline using Modified Abe Solvatochromic Model and Quantum Chemical Calculations

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ABSTRACT

The dipole moments and polarizabilities in various excited states of o-, m- and p-nitroanilines were estimated using Linder's variant of Abe solvatochromic model. The ground and excited state dipole moments of these molecules were computed from experimental and theoretical studies using solvatochromic technique and Density Functional Theory (DFT) respectively. The trend observed for the various excited states dipole moments of the o-, m- and p- isomers of nitroaniline follow the order ortho>meta>para. The excited state polarizabilities obtained for the electronic transitions in each of the compounds are reflective of the oscillator strength f values for these transitions. Also, the excited singlet-state dipole moments obtained were higher than the calculated ground state dipole moments which shows that the excited singlet-state is more polar than the ground state for all the compounds studied. The effects of solvent manifest in form of enhancement to the electronic intensities. The results of the present analysis show internal consistency and agree reasonably with Abe's theory.

Keywords: excited states, solvatochromic model, nitroaniline, oscillator strength, polarizabilities

1. INTRODUCTION

Extensive studies on the estimation of excited state dipole moments and polarizabilities using various solvatochromic model of electronic absorption bands have been reported [1-9]. However, there appear to be large dispersions in the reported values of electric dipole moments and polarizabilities of some molecules using solvatochromic theories proposed by some authors [10-12]. This is because in practice, the applications of such theories are often made under the assumptions that may be limited in validity or scope.

For instance, several arguments on the approximation of McRae's theory of

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solvatochromic shift and its use in determining electric dipole moments have appeared [14-15]. Also, Prabhumirashi and Kunte,[16] in their study have expressed doubts about the suitability of Abe’s rigorous theory in determining the excited state electric dipole moments and polarizabilities of some molecules, a situation that seems to emphasize the need for a reappraisal of the applicability of Abe’s solvatochromic theory.

Xu *et al.*, in 2009 [17] theoretically calculated the ground and first excited states of some 7-phenylamino-substituted coumarin compounds using Time-dependent density function theory (TD-DFT) methods. The effects of solvent on both the ground state and the first excited using self-consistent isodensity polarized continuum model were also investigated. The predicted spectra are in agreement with the experimental data. Similarly, the dipole moments of the ground and lowest electronically excited singlet state of 5-methoxyindole was determined by means of optical Stark spectroscopy in a molecular beam [18]. The effects of solvent polarity on ground and excited-state dipole moments of chlorogenic acid (CGA) and caffeic acids (CA)) was investigated experimentally using Bakhshiev, Kawski-Chamma-Viallet and Reinhardt equations and theoretically by Density Functional Theory (DFT) respectively [19].

In the present work, we apply Linder’s variant of Abe’s solvatochromic theory in determining the electric dipole moments and polarizabilities of o-, m- and p-nitroaniline.

2. EXPERIMENTAL

O-, m- and p-nitroaniline, cyclohexane, n-hexane, dichloromethane and chloroform are the products of Tokyo Kassei (Japan) and are of spectroscopic grades. Methanol, propan-1-ol, ethanol, 1, 4-dioxane and acetonitrile were obtained from British Drug House Ltd. and were redistilled several times.

Electronic spectra of dilute solutions of o-, m- and p-nitroaniline in the concentration range of 10^{-5}-10^{-4} M were determined with Schimadzu UV-1650 double beam spectrophotometer coupled with UV-probe® 2.31 version, operated in the wavelength region 190-450nm. All other experimental conditions are as been described previously by Iweibo, *et.al* [6]. Molar absorptivities and integrated absorption coefficients are determined by deconvolution of the spectra obtained as described by Iweibo, *et.al* [20]

2.1. Theoretical background

The Abe’s expression [10] which relates the transition energy in solution (hv_s) to that of the vapour (hv_v) and to the van der Waals interaction energies is given in equation 1 below

$$hv_s = hv_v - \left\{ \frac{2}{3} \frac{\left(\mu^{*2}_{a} - \mu_a^2\right)}{dkT} + \left(\alpha_a{}^{*} - \alpha_a\right) \right\} \sum_{i=1}^{N} \frac{\mu_{bi}^2}{dr_{abi}^6} - \left\{ \frac{\left(\mu^{*2}_{a} - \mu_a^2\right)}{d} \right\} + \frac{3}{2} \left\{ \frac{\alpha_a^{*} I_b}{1 + {}^{I_b}\!/_{I_a^{*}}} - \frac{\alpha_a I_b}{1 + {}^{I_b}\!/_{I_a}} \right\} \sum_{i=1}^{N} \frac{\alpha_{bi}}{r_{abi}^6} \quad (1)$$

where α, I and μ are electric dipole polarizability, ionization potential, and electric dipole moment respectively; Quantities with the asterisks(*) indicate those in excited states while those without are in ground state, k and T are the Boltzmann constant and absolute temperature of the solution respectively, h is the Planck’s constant and v is the frequency of the electronic transition,

$d=4\pi\varepsilon_{o}$, ε_o is the permittivity of the vacuum; subscripts *s* and *v* denote the solution and vapour phase respectively; *r* is the van der Waals intermolecular distance between the centers of the solute and solvent molecules and the summation is extended over *N* solvent molecules interacting with the solute.

To satisfy the statistical criteria for graphical analysis, equation 1 is rearranged to the following linear regression form.

$$Y = \frac{\left(\mu^{*2}_{a} - \mu_a^2\right)}{d} X_1 + \alpha_a^* X_2 \qquad (2)$$

$$\frac{Y}{X_1} = \frac{\left(\mu^{*2}_{a} - \mu_a^2\right)}{d} + \alpha_a^* \frac{X_2}{X_1} \qquad (3)$$

$$\frac{Y}{X_2} = \frac{\left(\mu^{*2}_{a} - \mu_a^2\right)}{d} \frac{X_1}{X_2} + \alpha_a^* \qquad (4)$$

$Y, \frac{Y}{X_1} \frac{Y}{X_2}$ in equations (2) - (4) respectively are dependent variables while X_1 and X_2 in equation (2), $\frac{X_2}{X_1}$ in equation (3) and $\frac{X_1}{X_2}$ in equation (4) the independent variables.

Mathematical definition of the variables in equations (2) – (4) are

$$Y = \left(hv_s - hv_v\right) + \alpha_a X_3 \qquad (5)$$

$$X_1 = \left(\frac{2}{3}\frac{\mu_b^2}{dkT} + \alpha_b\right) r_{ab}^{-6} \qquad (6)$$

$$X_2 = \left(\frac{\mu_b^2}{d} + \frac{3}{2}\frac{\alpha_b I_b}{\left(1 + {}^{I_b}\!/\!{}_{I_a^*}\right)}\right) r_{ab}^{-6} \qquad (7)$$

$$X_3 = \left(\frac{\mu_b^2}{d} + \frac{3}{2}\frac{\alpha_b I_b}{\left(1 + {}^{I_b}\!/\!{}_{I_a}\right)}\right) r_{ab}^{-6} \qquad (8)$$

where $I_a^* = I_a - h\nu_v$ In the application of Linder's [11] variant of equation (1), $Y = 2\left(hv_s - hv_v\right) + \alpha_a X_3$ in equations (2) - (4) while other variables retain their definitions.

Table 1 shows the molecular data used for the generation of Y, X_1 and X_2 for the least square and graphical analyses of data. The data on vapour phase transition frequencies for the three isomers were obtained from difference method as described by Millefiori [21].

2.2. Computational details

Quantum chemical calculations of the ground state molecular structures and geometry optimization of o-nitroaniline, m-nitroaniline and p-nitroaniline were carried out using Spartan 10 software package [22]. The ground and first excited state geometries, electric dipole polarizabilities, dipole moments and energy gap of the compounds in vacuum and methanol were theoretically predicted from *ab initio* calculations using restricted Hatree-Fock density functional theory (HF-DFT) applying B3LYP functional with 6-31G* basis set.

3. RESULTS AND DISCUSSION

3.1. Solvent effects on transition Energies

Table 2 shows the electronic absorption maxima of the three isomers of nitroanilines in some representative solvents and in vapour phase. Also, the transition intensities are reported in form of molar absorptivity and oscillator strengths in different solvents.

Figure 1-3 presents the electronic absorption spectra of the isomers, illustrating the interplay of the complementary roles of electron-donor substituent (the amino group) and the electron-withdrawing substituent (the nitro-group) on the benzene spectra.

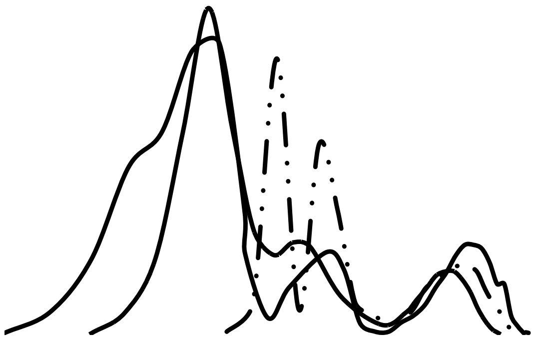
Table 1: Summary of data used for the determination of molecular (spherical) radii, polarizability and other solvent properties

	o-nitroaniline	m-nitroaniline	p-nitroaniline
I (eV)	8.58**[25]**	8.69**[25]**	8.85[25]
r_a (x 10^{-8} cm)	3.68*	3.68*	3.68*
r_{aw} (x 10^{-8} cm)	3.11**	3.11**	3.11**
α_0 (x10^{-24} cm^3)	15.1 **[25]**	15.1 **[25]**	15.1 **[25]**
μ_g (D)	4.27[16]	4.88[16]	6.30[16]

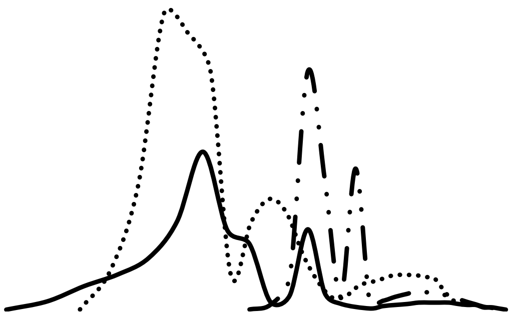
Ref. [16], Ref. [25], *computed from the density of 1.101Kgdm^{-3}
** computed from van der Waals’ volume.

Table 2: Summary of observed absorption bands of Compounds in different Solvents

Compounds and Transitions		**Hexane**			**Methanol**			**Chloroform**		
	$\bar{\nu}_v (cm^{-1})$	$\bar{\nu}_s$	f	ε_{max} (x10^3) M^{-1} cm^{-1}	$\bar{\nu}_s$	f	ε_{max}(x10^3) M^{-1} cm^{-1}	$\bar{\nu}_s$	f	ε_{max} (x10^3) M^{-1} cm^{-1}
o-nitroaniline										
$S_0 \rightarrow S_1$	28169	26610	0.125	5.17	24536	0.165	9.48	24979	0.142	5.56
$S_0 \rightarrow S_2$	38461	37833	0.102	7.58	35305	0.149	7.57	35899	0.125	15.79
$S_0 \rightarrow S_3$	45248	44022	0.212	27.19	43208	0.556	31.85	38999	0.420	22.97
m-nitroaniline										
$S_0 \rightarrow S_1$	30675	28233	0.062	3.51	27284	0.081	0.72	27126	0.081	5.14
$S_0 \rightarrow S_2$	40000	37895	0.128	11.22	35348	0.106	8.14	32178	0.136	8.49
$S_0 \rightarrow S_3$	45455	44875	0.428	30.05	42292	0.356	16.00	35348	0.281	24.14
p-nitroaniline										
$S_0 \rightarrow S_1$	-	31300	0.484	22.42	26960	0.640	21.18	28500	0.582	24.97
$S_0 \rightarrow S_2$	34247	42580	0.106	11.90	41500	0.112	12.75	42300	0.102	12.64
$S_0 \rightarrow S_3$	45662	44180	0.141	17.85	43990	0.138	18.82	-	-	-



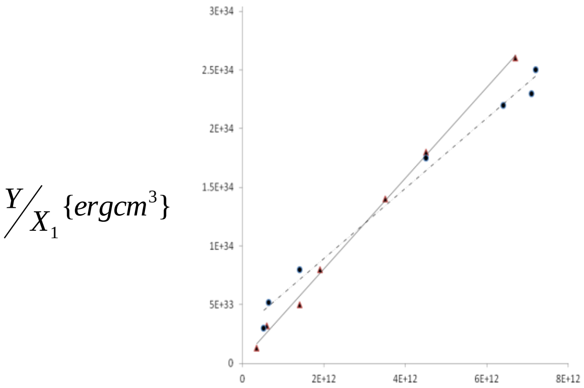
***a. o*-nitroaniline**



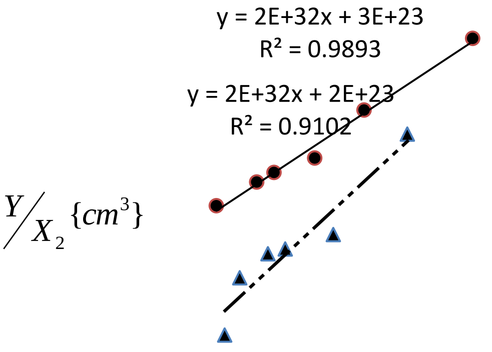
***b. m*-nitroaniline**

c. *p*-nitroanilne

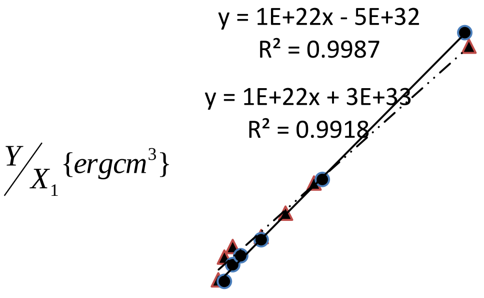
Figure 1: Electronic absorption spectra of nitroanilines in Methanol (————), chloroform (··········), n-hexane (—··—··—··)



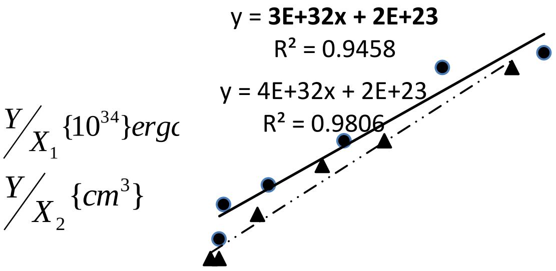
(ai) ***o*-nitroaniline** $X_2/X_1\,(erg)$



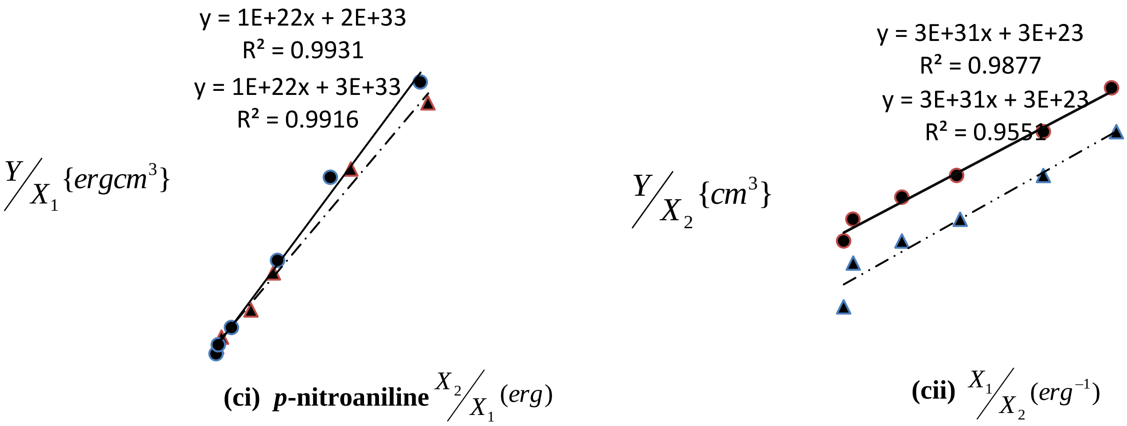
(aii) $X_1/X_2\,(erg^{-1})$



(bi) ***m*-nitroaniline** $X_2/X_1\,(erg)$

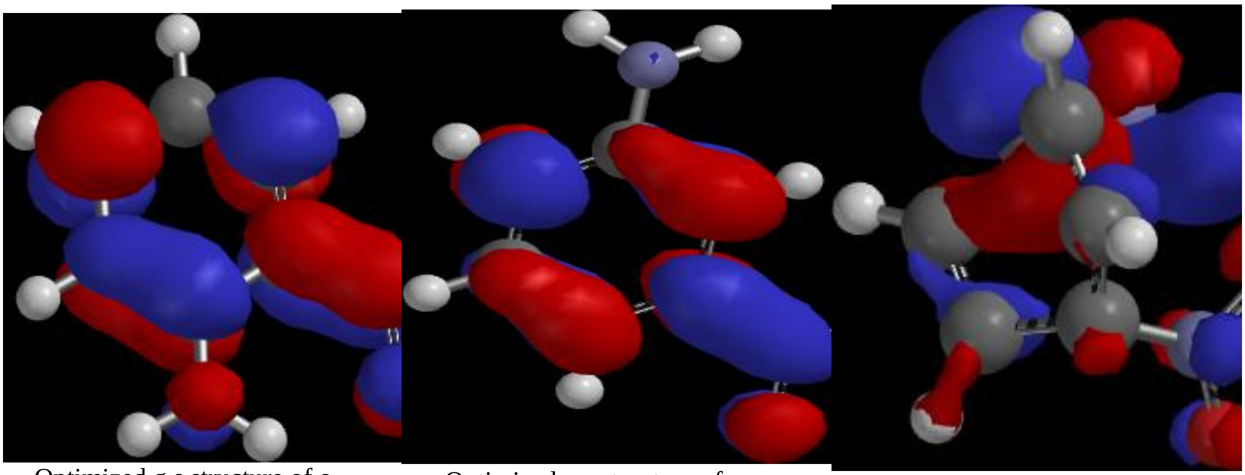


(bii) $X_1/X_2\,(erg^{-1})$



(ci) ***p*-nitroaniline** $^{X_2}/_{X_1}(erg)$ **(cii)** $^{X_1}/_{X_2}(erg^{-1})$

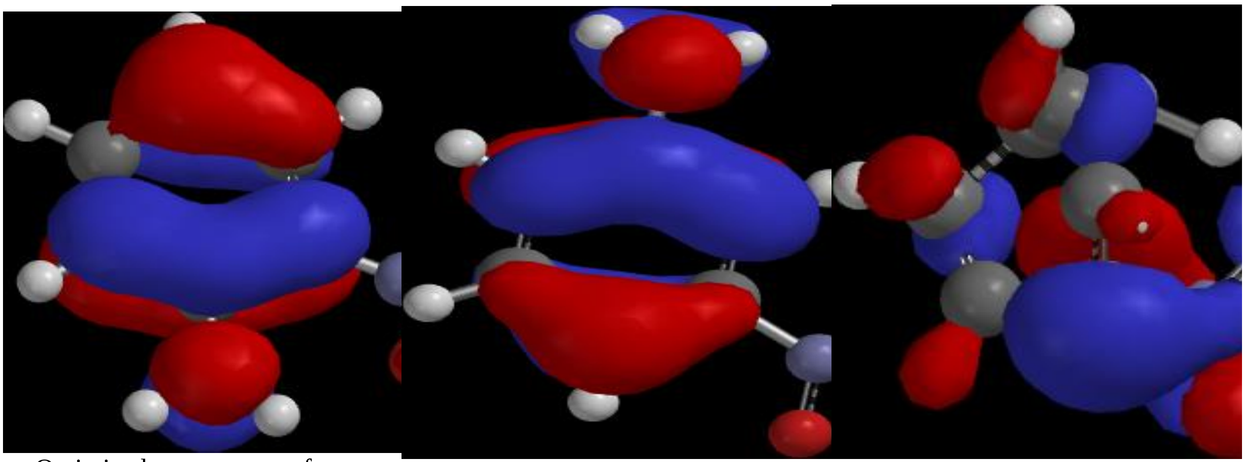
Figu Plots of data on solvent frequency shift of the $S_0 \rightarrow S_1$ bands in (a) o- nitroaniline (b) m-nitroaniline (c) p-nitroaniline according to equation s 3 and 4.



Optimized g.s structure of o-nitroaniline

Optimized g.s structure of m-nitroaniline

Optimized g.s structure of p-nitroaniline



Optimized e.s structure of o-nitroaniline

optimized e.s structure of m-nitroaniline

optimized e.s structure of p-nitroaniline

Figu Optimized ground and excited state structures of o-, m- and p-nitroaniline

Figure 1 presents the electronic absorption spectra of the o-nitroaniline isomers; the $S_0 \rightarrow S_1$ transition occurs at 24536cm^{-1}, 24979cm^{-1} and 26610cm^{-1} in methanol, chloroform and hexane respectively. Also, the $S_0 \rightarrow S_2$ transition occurs at 35305cm^{-1}, 35899cm^{-1} and 37833cm^{-1} in methanol, chloroform and hexane respectively. It was observed that the absorption bands in both transitions are red-shifted in accordance with the Bayliss theory of solvent polarities and so do the intensities of each band in the representative solvents. The $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions are both quantum-mechanically allowed but overlap forbidden as reflected in their intensities.

The $S_0 \rightarrow S_3$ transition occurs at 43208cm^{-1}, 38999cm^{-1} and 44022cm^{-1} in methanol, chloroform and hexane respectively. The absorption band in chloroform is blue-shifted relative to a much polar solvent like methanol. However, the $S_0 \rightarrow S_3$ transition in methanol has a broad band and much intense than others and it has a shoulder towards blue at 49648cm^{-1}. The $S_0 \rightarrow S_3$ bands are both quantum-mechanical and overlap allowed in all the solvents.

Similar trends observed for $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_3$ transitions in o-nitroaniline were also observed in m-nitroaniline. However, the $S_0 \rightarrow S_1$ transition in m-nitroaniline are both quantum-mechanical and overlap forbidden and the $S_0 \rightarrow S_3$ band in methanol has a shoulder towards the red at 39220cm^{-1}.

For p-nitroaniline, the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions follow the same trends observed in o- and m-aniline. However, the $S_0 \rightarrow S_3$ transition in chloroform is obscured due to non-transparency of most halogenated hydrocarbon in that region of the UV light. All the transitions in p-nitroaniline are both quantum-mechanical and overlap allowed as reflected in their intensities in figure 3. These spectra features are in agreement with those reported [16, 21, 23, and 24].

3.2. Solvent effects on oscillator strength

Generally, the oscillator strength of an electronic transition of any given compound in a series of solvents increases with increase in solvent polarity. This is true for most transitions in this study and the trend is in harmony with expectation, because in polar solvents, all the van der Waal`s interaction between solute and solvent (the dispersion interaction inclusive) are operative in the perturbation of the oscillator strength whereas in non polar solvents only the dispersion interaction terms exist [26]. As shown in table 2, the oscillator strength, *f*, obtained ranged from 10^{-2} for the forbidden electronic transition to approximately 1.0 for fully allowed transition. The experimentally determined oscillator strength for two of these isomeric nitroanilines compounds in solution follows the general trend

$$f_{(s_0 \rightarrow s_1)} < f_{(s_0 \rightarrow s_2)} < f_{(s_0 \rightarrow s_3)}$$

However, deviation occurs in p-nitroaniline and the observed trend is

$$f_{(s_0 \rightarrow s_2)} < f_{(s_0 \rightarrow s_1)} < f_{(s_0 \rightarrow s_3)}$$

3.3. Excited state electric dipole moments and polarizabilities

As shown in table 3, the magnitude of the excited state polarizabilities of the compounds follows the order $\alpha_{(S_0 \rightarrow S_3)}$ > $\alpha_{(S_0 \rightarrow S_2)}$ > $\alpha_{(S_0 \rightarrow S_1)}$ which is the order of the oscillator strengths of these transitions. This order of polarizability conforms to expectation, since by definition, the polarizability of a given state *i* is proportional to the square of the modulus of the transition moment from state *I* to all other states, i.e. $I\ \alpha \left|M_{ij}\right|^2 = <\mu_i|e_i r_i|\mu>^2$. Expectedly, the $\Delta\alpha$ values also follow the order of the excited state polarizabilities for the various transitions in a given compound. Comparison of the excited state polarizabilities and moments obtained from computation of solute and solvent molecular radii as was done by Abe [10] and those obtained from van der Waals' molecular radii as presented in this work indicate clearly that the latter yields excited state polarizabilities much lower in value.

Computation with van der Waals' radii significantly minimizes the differences in the values of electric dipole polarizabilities and moments obtained with Linder's variant of Abe's equations which are comparable with values obtained from quantum chemical calculations presented in table 4. However, satisfactory comparison could not be drawn between the values obtained using the Linder's variant of Abe's solvatochromic equations and the values obtained from the quantum chemical/ molecular orbital calculations because the former considered each transition in each isomer separately. This is not unconnected with some inherent assumptions made in the Abe's solvatochromic equation. Despite that, the equation in its modified form as presented in this paper reveals that the perturbing electric field is a direct measured quantity and should be presumably lack the uncertainties associated with the determination of r_{ab}^3 in solvatochromic field.

Table 3: Summary of excited state electric dipole moments and polarizabilities and for the compounds

Compounds and Transitions	(D) μ_e	(10^{-24} cm^3) α_e	(D) $\Delta\mu$	(10^{-24} cm^3) $\Delta\alpha$
o-nitroaniline				
$S_0 \rightarrow S_1$	7.31^*	48.8^*	3.04	33.7
	4.93^{**}	29.3^{**}	0.66	14.2
$S_0 \rightarrow S_2$	6.92^*	53.5^*	2.65	38.4
	4.69^{**}	32.6^{**}	0.42	17.5
$S_0 \rightarrow S_3$	5.98^*	67.2^*	1.71	52.1
	4.43^{**}	40.4^{**}	0.16	25.3
m-nitroaniline				
$S_0 \rightarrow S_1$	6.96^*	50.5^*	2.08	35.4
	5.90^{**}	31.7^{**}	1.02	16.6
$S_0 \rightarrow S_2$	6.05^*	72.8^*	1.17	57.7
	5.72^{**}	39.4^{**}	0.84	24.3
$S_0 \rightarrow S_3$	5.99^*	89.1^*	1.11	74.0
	5.20^{**}	52.9^{**}	0.32	37.8
p-nitroaniline				
$S_0 \rightarrow S_1$	8.36^*	85.9^*	2.06	70.5
	6.94^{**}	49.4^{**}	0.64	34.3
$S_0 \rightarrow S_2$	7.52^*	42.3^*	1.22	27.2
	6.78^{**}	27.2^{**}	0.48	12.1
$S_0 \rightarrow S_3$	6.91^*	54.8^*	0.61	39.7
	6.49^{**}	34.7^{**}	0.19	19.6

* Results obtained by computation of the molecular radii from molar mass and density
** Results obtained by computation with van der Waal's molecular radii.

Tab[illegible] Calculated Results at B3LYP/6-31G* basis sets of optimized structures of studies compounds

Str[illegible]**e-solvent**	**Energy(au)**	**E_{LUMO} (eV)**	**E_{HOMO} (eV)**	**ΔE(eV)**	**μ (eV)**	**α(Å^3)**
o-NA-Vacuum	-492.10	-2.17	-6.06	3.89	4.74	51.02
m-NA -Vacuum	-492.11	-2.24	-6.14	3.90	5.65	51.10
p-NA-Vacuum	-492.11	-1.96	-6.25	4.29	7.12	50.99
o-NA- methanol	-492.12	-2.37	-5.86	3.49	7.11	51.13
m-NA-methanol	-492.12	-2.59	-5.77	3.18	7.59	51.27
p-NA-methanol	-492.13	-2.23	-5.80	3.57	11.68	51.17

o-NA, m-NA, and p-NA are o-nitroaniline, m-nitroaniline and p-nitroaniline respectively.

4. CONCLUSION

We have determined the excited state electric dipole moments and polarizabilities of o-, m-and p-nitroaniline using Linder's variant of Abe solvatochromic model and quantum chemical calculations**.** We found that the values of electric dipole moments and excited state polarizabilities are reflective of electronic intensities (in term of oscillator strength) for various transitions in line with the approximate theory [27, 28]. Finally, we observed that the excited singlet-state dipole moments were higher than the calculated ground state dipole moments and this confirmed that the excited singlet-state is more polar than the ground state for the compounds under consideration.

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تعیین گشتاورهای دوقطبی الکتریکی حالت برانگیخته و قطبش پذیری نیتروآنیلین ایزومری موقعیتی با استفاده از مدل حل شده Abe Solvatochromic و محاسبات شیمیایی کوانتومی

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چکیده

گشتاورهای دوقطبی و قطبش پذیری در حالت‌های مختلف برانگیخته -o، -m و -p-نیتروآنیلین‌ها با استفاده از مدل Linder مدل Abe solvatochromic برآورد شد. گشتاورهای دوقطبی حالت زمین و برانگیخته این مولکول‌ها به ترتیب با استفاده از تکنیک solvatochromic و نظریه تابعی چگالی (DFT) از مطالعات تجربی و نظری محاسبه شدند. روند مشاهده شده برای ممان‌های دوقطبی حالت‌های برانگیخته مختلف ایزومرهای -o، -m و -p از نیتروآنیلین از ترتیب para<meta<ortho پیروی می‌کند. قطبش پذیری حالت برانگیخته به دست آمده برای انتقال‌های الکترونیکی در هر یک از ترکیبات، منعکس کننده مقادیر f قدرت نوسانگر برای این انتقال است. همچنین گشتاورهای دوقطبی تک حالت برانگیخته به‌دست‌آمده بیشتر از گشتاورهای دوقطبی حالت پایه محاسبه‌شده بود که نشان می‌دهد حالت تک حالت برانگیخته قطبی‌تر از حالت پایه برای همه ترکیبات مورد مطالعه است. اثرات حلال به شکل افزایش شدت‌های الکترونیکی آشکار می‌شود. نتایج تحلیل حاضر همخوانی درونی را نشان می‌دهد و به طور منطقی با نظریه آبه موافق است.

کلید واژه‌ها: حالت‌های برانگیخته، مدل سولواتوکرومی، نیتروآنیلین، قدرت نوسانگر، قطبش پذیری

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