EFFECT OF SOLVENT POLARITY ON THE ABSORPTION AND FLUORESCENCE SPECTRA OF NICOTINAMIDE: DETERMINATION OF GROUND AND EXCITED STATE DIPOLE MOMENTS†

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Nicotinamide (NIC) is an amide-form vitamin with a carboxamide group at b positions that is involved in a variety of biological activities. The drugs contain functional groups which control the type and degree of interaction with different solvents. In this research, the ground and excited state dipole moments of nicotinamide (NIC) were estimated using solvatochromic effects and computational work. A general overview of solvent effects on the electronic absorption and fluorescence spectra of NIC is presented. In both spectra, pronounced solvatochromic effects were observed, and the shift of emission peaks was larger than the corresponding absorption spectra. The experimental ground state $\left(\mu_g\right)$ and excited state $\left(\mu_e\right)$ dipole moments of NIC are estimated from solvatochromic shifts of absorption and fluorescence spectra. The differences between the excited and ground state dipole moments determined by all the methods are quite similar. The HOMO-LUMO energy band gaps were calculated and found to be 5.566 eV. The excited state dipole moment is found to be higher than those of the ground state for all of the used methods, and it is attributed to the more polar excited state of NIC. Finally, the observed spectral properties, measured values of dipole moments, and electronic structures of NIC in different solvents provide important details about charge distribution and solute-solvent interactions that may be helpful in the investigation of these molecules in biological systems.

Keywords: Solvatochromic shift method, Ground state dipole moments, Excited state dipole moments, Nicotinamide
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Introduction

Vitamins are very important organic chemical compounds as a vital nutrient to sustain life due to their important role in normal metabolism processes, growth, and vitality [1]. Nicotinamide (3-pyridine-carboxamide, Vitamin B3) is a water-soluble pyridine derivative and amide form vitamin with a carboxamide group at position b that is involved in many biological activities [2-9]. It helps with diabetes treatment and prevention [6], skin appearance [10–12], energy metabolism, fatty acid synthesis, growth and development, signal transduction, and genome integrity [4,5,8]. Besides, it serves as an important functional group of coenzymes for NAD+ and NADP+ [13,14], which are involved in various chemical reactions including the production of energy in all types of cells [15,16], exhibit antioxidant, anti-inflammatory, and anticarcinogenic activities [2,7], and cytoprotective effects on neural and vascular tissues [17,18]. It is also applicable to different dietary foods, nutritional ingredients, and cosmetics [3].

The absorption and emission spectra of organic molecules are usually modified in solvation processes where the photon of light causes a redistribution of charges, leading to conformational changes in the excited state. The conformational changes induced by solvents in the electronic spectra of molecules can offer information on the local electric field acting on the spectrally active molecule. Thus, the exited dipole moment of an electronically excited molecule is an important property for providing information on the electronic and geometrical structure of the molecules [19,20], in designing non-linear materials [21] and new molecules, selecting best performance in analysis of specific applications, providing information about the nature of the excited states [22–24], determining emission energy as a function of the solvent polarity [22,23], and in parametrisation in quantum chemical procedures for these states [19]. The determination of the singlet excited-state dipole moment is based on the spectral shift caused either externally by electrochromism or internally by solvatochromism. The electrooptic methods (electrochromism) [25,26] are generally considered to be very accurate, but due to their limited use and restricted to relatively very simple molecules, the solvatochromic method is more preferable. The solvatochromic method is simpler and widely accepted [27–33]. It is based on a linear correlation between absorption and fluorescence maxima in different solvent polarity functions.

Several workers have conducted extensive experimental and theoretical studies on ground state and excited-state dipole moments using different techniques in a variety of organic fluorescent compounds [19,22,34-39]. In the present work, the ground and excited state dipole moments of NIC by the solvent perturbation method [28,30] have been determined from solvatochromic shifts using experimental and computational methods. However, there are no reports available in the literature on the determination of the dipole moment value of the compound investigated. Dipole moments

were estimated using Bakhshiev's [27], Kawaski–Chamma–Viallet [28–30] and Lippert–Mataga [31,32] equations and the quantum chemical method.

METHODS AND MATERIALS
Experimental details

Nicotinamide (NIC, Fig. 1) was purchased from Sigma-Aldrich Company and used for measurement without further purification. All the solvents were of spectroscopic grade and purchased from the Sigma-Aldrich Company.

Figure 1. Chemical structure of NIC

Electronic absorption spectra of the compounds were recorded using a Perkin-Elmer Lambda 19 UV-Vis spectrophotometry with double monocromator using a 1-cm path length quartz cuvette. The absorption spectra were recorded in the wavelength regions 200-500 nm, with a spectral band width of 0.1 nm and a scanning speed of 600 nm/min. The steady-state fluorescence spectra were recorded by Fluoromax-4 spectrophotometer (Horiba). The emission spectra were recorded by exciting the sample at its longest absorption maximum. The absorption and emission measurements were performed at room temperature, keeping the concentration of the molecule very low for the fluorescence spectra measurement. The solvent polarity functions were calculated from the relative permittivity and refractive index of the solvents, and the values are shown in Table 1.

Table 1. Solvent functions $f(\varepsilon_r, n)$, $\phi(\varepsilon_r, n)$, F_{L-M}, F_{K-C-V} and F_B, used in the Bakhshiev, Kawski–Chamma–Viallet, Lippert-Mataga and Reichardt equations, respectively

Solvent	ε^a	n^a	f^b	ϕ^b	$F_{L-M}{}^c$	$F_{K-C-V}{}^d$	$F_B{}^e$
Water	80.10	1.3325	0.91375	0.2265	0.32028	0.683392	0.913758
Ethanol	24.55	1.3614	0.81293	0.2459	0.28874	0.652459	0.812933
Acetonitrile	37.50	1.3404	0.86408	0.2318	0.30682	0.663891	0.864083
Butanol	17.84	1.399	0.75370	0.2711	0.26433	0.647996	0.753704
Methanol	33	1.328	0.85573	0.2234	0.30894	0.651335	0.855732

[a] ε = relative permittivity and n=refractive index.

[b] Bilot-Kawski solvent functions in Eqns. (3&4)

[c] Lippert-Mataga solvent function in Eqn. (17).

[d] Kawski-Chamma-Viallet solvent function in Eqn. (18)

[e] Bakhshiev solvent function in Eqn. (19).

THEORETICAL BACKGROUND
Bilot–Kawski method

Based on Onsager's reaction field theory, which assumes a spherical structure of the molecules within a cavity radius 'a' and employing the simplest quantum mechanical second order perturbation theory of absorption ($\tilde{v}_a$) and fluorescence ($\tilde{v}_f$) band shifts in various solvents of different relative permittivity (ε_r) and refractive index (n), the equations for the dipole moments were calculated [28,31,32,40-46]. According to Bilot and Kawski [28,41], the equations related to the difference and sum of wavenumbers of absorption and fluorescence are expressed as Eqns. (1 &2).

$$\tilde{v}_a - \tilde{v}_f = m_1 f(\varepsilon_r, n) + \text{constant} , \tag{1}$$

$$\tilde{v}_a + \tilde{v}_f = -m_2 \phi(\varepsilon_r, n) + \text{constant} , \tag{2}$$

where the solvent polarity parameters $f(\varepsilon_r, n)$, and $\phi(\varepsilon_r, n) = f(\varepsilon_r, n) + 2g(n)$ [40,43,47] are expressed as Eqns. (3 & 4), respectively.

$$f(\varepsilon_r, n) = \frac{2n^2 + 1}{n^2 + 2}\left(\frac{\varepsilon_r - 1}{\varepsilon_r + 2} - \frac{n^2 - 1}{n^2 + 2} \right) , \tag{3}$$

$$g(n) = \frac{3}{2}\left(\frac{n^4 - 1}{(n^2 + 2)^2} \right) . \tag{4}$$

The parameters m_1 and m_2 which can be determined from the slope of the straight line of Eqns. (1&2) are given by:

$$m_1 = \frac{2(\mu_e - \mu_g)^2}{hca^3}, \tag{5}$$

$$m_2 = \frac{2(\mu_e^2 - \mu_g^2)}{hca^3}, \tag{6}$$

where h and c are the plank's constant and the velocity of light in vacuum respectively; $a = (3M / 4\pi\delta N)^{1/3}$ with the relative molecular mass of the solute molecules (M), the density (δ) and Avogadro's number (N).

Assuming the symmetry of the solute molecule remains unchanged upon electronic transition and the dipole moment states are parallel, the values of the ground and excited dipole moments from Eqns. (5&6) can be obtained as [40,43,47],

$$\mu_g = \frac{|m_2 - m_1|}{2}\left(\frac{hca^3}{2m_1}\right)^{1/2}, \tag{7}$$

$$\mu_e = \frac{|m_2 + m_1|}{2}\left(\frac{hca^3}{2m_1}\right)^{1/2}, \tag{8}$$

$$\frac{\mu_e}{\mu_g} = \frac{|m_2 + m_1|}{|m_2 - m_1|} \qquad \text{for } m_2 > m_1. \tag{9}$$

Moreover, if the ground state and excited state dipole moments are not parallel to each other, the angle between the two dipole moments can be determined [42] as

$$\cos\theta = \frac{1}{2\mu_g\mu_e}\left[\left(\mu_g^2 + \mu_e^2\right) - \frac{m_1}{m_2}\left(\mu_e^2 - \mu_g^2\right)\right]. \tag{10}$$

Lippert–Mataga, Kawski–Chamma–Viallet and Bakhshiev methods

The electric dipole moment of a polar solute polarizes the solvent so that the solute itself experiences an electric field, the reaction field, which is proportional to the solute dipole moment in the ground and excited states. Such proportionalities for the difference and sum of absorption and fluorescence maxima maximum wavenumber have been defined by the following independent equations [30-32,48] used for the estimation of ground and excited state dipole moments:

$$\tilde{v}_a - \tilde{v}_f = m_3 F_{L-M}(\varepsilon_r, n) + \text{constant}, \tag{11}$$

$$\frac{\tilde{v}_a + \tilde{v}_f}{2} = -m_4 F_{K-C-V}(\varepsilon_r, n) + \text{constant}, \tag{12}$$

$$\tilde{v}_a - \tilde{v}_f = m_5 F_B(\varepsilon_r, n) + \text{constant}, \tag{13}$$

m_3, m_4 and m_5 are the slopes of the linear relationships corresponding to Eqns. (11-13), are given by;

$$m_3 = \frac{2(\mu_e - \mu_g)^2}{hca^3} \tag{14}$$

$$m_4 = \frac{2(\mu_e^2 - \mu_g^2)}{hca^3} \tag{15}$$

$$m_5 = \frac{2(\mu_e - \mu_g)^2}{hca^3} \tag{16}$$

F_{L-M} [31,32], F_{K-C-V} [30] and F_B [48] are solvent polarity functions corresponding to Lippert–Mataga, Kawski–Chamma–Viallet and Bakhshiev methods and are given as:

$$F_{L-M}(\varepsilon_r, n) = \left(\frac{\varepsilon_r - 1}{2\varepsilon_r + 1} - \frac{n^2 - 1}{2n^2 + 1}\right) \tag{17}$$

$$F_{K-C-V}(\varepsilon_r, n) = \frac{2n^2+1}{2(n^2+2)}\left(\frac{\varepsilon_r-1}{\varepsilon_r+2} - \frac{n^2-1}{n^2+2}\right) + \frac{3(n^4-1)}{2(n^2+2)^2} \tag{18}$$

$$F_B(\varepsilon_r, n) = \frac{2n^2+1}{n^2+2}\left(\frac{\varepsilon_r-1}{\varepsilon_r+2} - \frac{n^2-1}{n^2+2}\right) \tag{19}$$

Computational Methods

The ground state dipole moment ($\vec{\mu}_g$) of the three compounds was theoretically calculated using the Gaussian 09 program and analysed with the help of Gauss View software [49]. The calculations and ground state geometries optimization were performed at a density functional theory (DFT) level of theory by employing Becke's three parameter (local, non-local, Hartee-Fock) hybrid exchange functional (B3LYP) and the basis set 6–311G(d,p).

RESULTS AND DISCUSSION

Determination of the photophysical and photochemistry of different drug compounds is useful for various applications. The values of ground- and excited-state dipole moments of the molecules provide information about the change in electronic distribution of the excited molecule [22,23]. It elucidates the nature of the excited state of the molecules as it reflects the charge distribution in the molecule [22,23,50]. Furthermore, the experimental data on dipole moment can be used to parameterize quantum chemical procedures for these states [19]. The excited dipole moments of the fluorescent molecules have also been used to determine emission energy as a function of the solvent polarity function [22,23].

Solvent effects on UV-Vis absorption and fluorescence spectra of Nicotinamide

The absorption and fluorescence emission spectra of NIC were recorded in solvents of different solvent parameters with the corresponding solvent polarity values as in Table 1. Figs. 2&3 shows the typical absorption and fluorescence spectra of NIC obtained in different solvents. The UV-Vis absorption spectra of NIC are characterized by their maximum absorption band, which corresponds to HOMO → LUMO mainly due to $\pi \rightarrow \pi^*$ orbital transition. And, the fluorescence spectra of NIC undergoes an average of a red shift as it increasing in solvent polarity. Fig. 2 shows an exchange of order in water and acetonitrile, and in methanol and ethanol as solvent polarity increases, most possibly due to the influence of an intermolecular association and/or solute-solvent interactions.
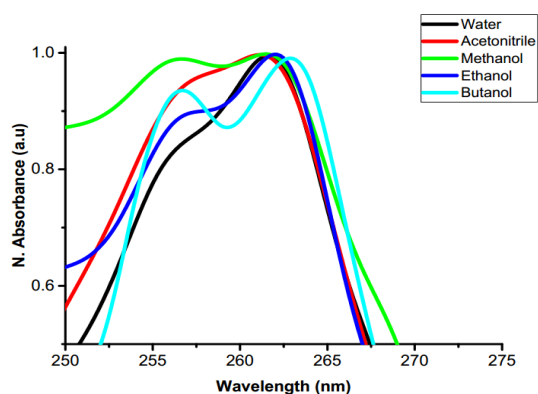

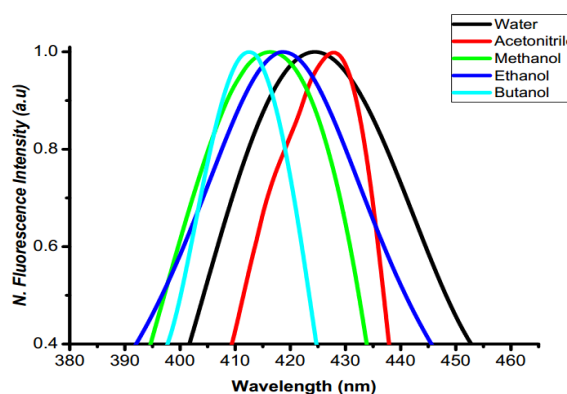**Figure 2.** Absorbance spectra of NIC in different solvents

Figure 3. Florescence spectra of NIC in different solvents

As compared to the absorption spectra, a large spectral shift was observed in the emission spectra as shown in Table 2. The lesser spectral shifts in the absorption maxima compared with the fluorescence spectra of the compound implies that the ground state energy distribution may not be affected to a greater extent, possibly due to the less polar nature of the compound in the ground state rather than in the excited state.

Table 2. Difference, Sum and mean of Peak absorption and emission spectra of Nicotinamide in different polar solvents

Solvent	$\tilde{v}_a$	$\tilde{v}_f$	$\tilde{v}_a - \tilde{v}_f$	$\tilde{v}_a + \tilde{v}_f$	$(\tilde{v}_a + \tilde{v}_f)/2$
WATER	3822630	2358491	1464139	6181121	3090560
ETHANOL	3816794	2392344	1424449	6209138	3104569
ACETONITRILE	3831418	2336449	1494969	6167866	3083933
BUTANOL	3802281	2427184	1375097	6229466	3114733
METHANOL	3816794	2403846	1412948	6220640	3110320

$\tilde{v}_a$, absorption maximum in cm^{-1}; $\tilde{v}_f$, fluorescence maximum in cm^{-1}

The absorption and fluorescence emission data of NIC in solution also provided reliable information about the solvation effects in the ground and excited states. From Table 2, we observe that the magnitude of Stokes shift for the compound increased with increasing solvent polarity. The large magnitude of the Stokes shift indicates that the excited state geometry of the compound could be different from that of the ground state and that there will also be an increase in dipole moment on excitation. Furthermore, these solvatochromic data can also provide information to identify the possible orbital transition of the compounds, namely $\pi \rightarrow \pi^*$ or $n \rightarrow n^*$ etc. The data reveals that, with an increase in solvent polarity, the electronic emission peak undergoes an average of red shift, confirmed as a $\pi \rightarrow \pi^*$ transition. Generally, the pronounced emission band shifts and increase in Stokes' shift values with an increase in solvent polarity indicate there is an increase in dipole moment on excitation.

Dipole Moments Calculation

To get a further insight into the solvatochromic behaviour of nicotinamide, the spectroscopic properties were correlated with the solvent polarity functions. From the slope of the Bilot-Kawski, Lippert-Mataga, Kawski-Chamma-Viallet and Bakhshiev equations, the ground and excited dipole moments were calculated. Figs. 4&5 shows the Stokes shift and the sum of the wavenumbers versus solvent polarity function for NIC using the Bilot-Kawski equations.
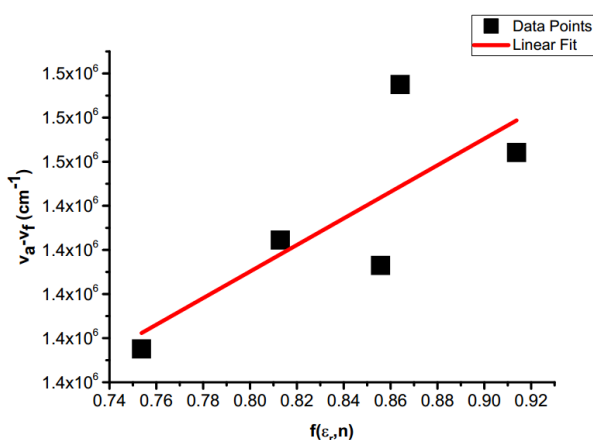

Figure 4. Plot of $\tilde{v}_a - \tilde{v}_f$ versus $f(\varepsilon_r, n)$ of NIC in different polar solvents using Bilot Kawski equation
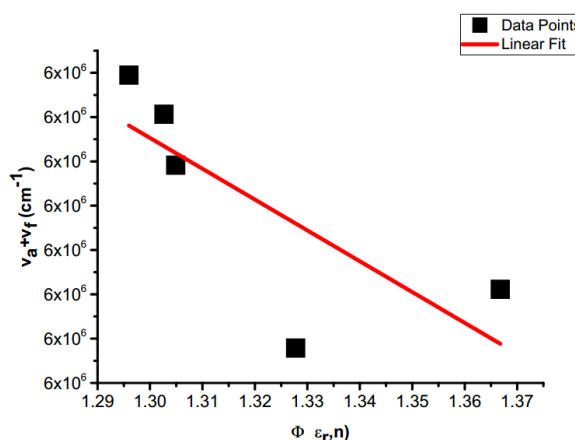

Figure 5. Plot of $\tilde{v}_a + \tilde{v}_f$ versus $\phi(\varepsilon_r, n)$ of NIC in different polar solvents using Bilot Kawski equation

Similarly, Figs. 6&7 are the plots of the Stokes shift and the mean of the wavenumbers versus the solvent polarity for Lippert-Mataga and Kawski-Chamma-Viallet equations respectively. The deviation of the data in Figs. 4, 5, 6 &7 could be from the influence of intermolecular association or solute-solvent interaction [51].
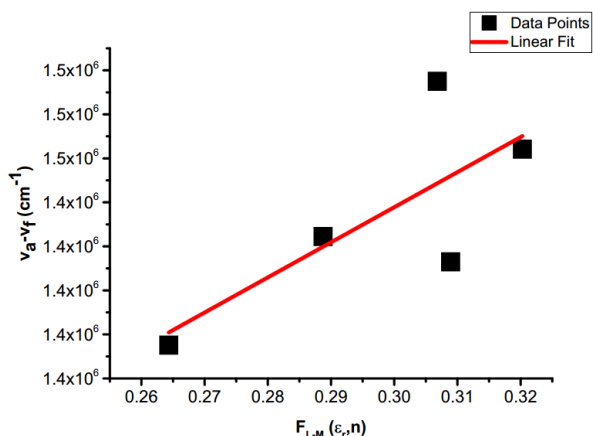

Figure 6. Plot of $\tilde{v}_a - \tilde{v}_f$ versus $F_{L-M}(\varepsilon_r, n)$ of NIC in different polar solvents using Lippert Mataga equation
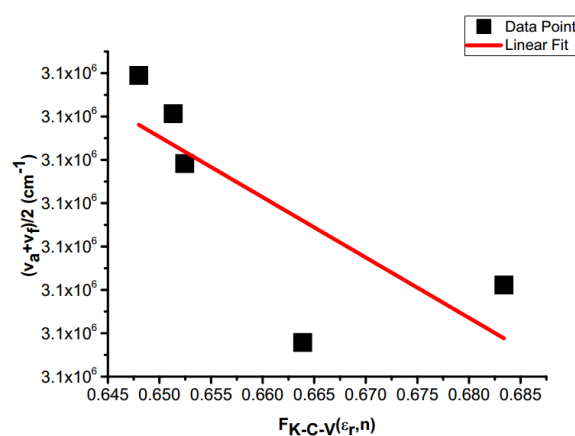

Figure 7. Plot of $(\tilde{v}_a + \tilde{v}_f)/2$ versus $F_{K-C-V}(\varepsilon_r, n)$ of NIC in different polar solvents using Kawski-Chamma-Viallet equation

From the slopes of the graphs of Figs. 4, 5, 6 & 7, the ground and excited state dipole moments were calculated and the values are as shown in Table 3.

Table 3. Ground state, excited-state dipole moments in Debye (D), and Onsager cavity radius 'a' ($\overset{\circ}{A}$), calculated by experimental and theoretical methods for Nicotinamide

a^a	μ_g^b	μ_e^c	$\Delta\mu_{B-K}^d$	$\Delta\mu_{L-M}^e$	μ_{gK-C-V}^f	$\Delta\mu_{gB}^g$	μ_g^h	μ_e^{h*}	θ^i	μ_g^j	μ_e^k	μ_s^l
2.258	0.02	0.254	0.234	0.364	0.064	0.216	1.48	1.87	0°	0.315	0.316	0.096

$1D = 3.33564 \times 10^{32} C.cm$

[a] calculated Onsager cavity radius

[b] Ground state dipole moment calculated according to Bilot-Kawski, Eqn. (7)

[c] Excited state dipole moment calculated according to Bilot-Kawski, Eqn. (8).

[d] Change of excited and ground dipole moments using Eqns. (7&8)

[e] Calculated change dipole moment according to Lippert-Mataga correlation, Eqn. (14).

[f] Calculated ground dipole moment according to Kawski-Chamma-Viallet method, Eqns. (15&7).

[g] Calculated change of dipole moment according to Bakhshiev correlation, Eqn. (16).

[h] calculated ground dipole moments from Gaussian 9 using #td b3lyp/6-311++g

[h*] calculated excited dipole moments from Gaussian 9 using #opt b3lyp/6-311++g

[i] Angle between ground and excited dipole moments using Eqn. (10)

[j] The value from reference ([51])

[k] The value from reference ([51])

[l] The value from reference ([51])

The calculated values of the ground and excited state dipole moments using Eqns. (7 &8), are 0.02 and 0.254 D. Due to the different assumptions and simplifications used by each method, the ground and excited state dipole moments that are estimated by different methods are not similar [60]. The change in dipole moments ($\Delta\mu$ =0.364) obtained using Lippert–Mataga Eqn. (14) is larger than the value obtained by other methods. This is due to the fact that the Lippert–Mataga equation neglected the polarizable nature of the solute molecules [55]. It has also been reported previouslythat the change in dipole moment obtained using the Lippert–Mataga equation is larger than the values calculated by other methods [55, 23, 40, 61]. Furthermore, the ground and excited E-nicotinamide results from individual stark lobe measurements were obtained and reported [51], $\mu_g = 0.315$ and $\mu_e = 0.316\,D$ using microwave spectrum. Because of the used solvents with different techniques and temperatures, the reported results by [51] are slightly larger than the results of this study using Bilot-Kawski of Eqn. (7&8). Thus, the results of the current study are better than the results previously reported by [51], because of the difference between the ground and excited state dipole moments required for solvatochromism. The results of the ground dipole moment in this study are also similar to the results obtained by [52], 0.0967 D on the surface of nicotinamide by the Helmholtz equation on the basis of surface excess values obtained from surface tension measurements and surface potential changes.

In general, the difference between the excited and ground state dipole moments ($\Delta\mu$) obtained by experimental and theoretical methods is moderately high, indicating that the excited dipole moment is greater than that in the ground state and also more polar than in the ground state.

Quantum Chemical Calculation

Figs. 8 (a-d) shows the HOMO-LUMO structures, the optimized structure with the dipole moment vector, and the total electron density with the electrostatic potential map (TED-ESP) for NIC using TD SCF-DFT-B3LYP-6-311G. It shows the spatial distribution of the electron cloud in three dimensions.

Table 3 shows the dipole moments determined in the gas phase by ab initio calculation using the Gaussian 09 software [49]. The dipole moments calculated by quantum chemical calculations in the gas phase were μ_g=1.48 D and μ_e=1.9D. The theoretical dipole moments are greater than the experimental results. This is because the dipole moments that are based on charge densities obtained from Eigen functions of the molecular orbital approximations are considerably higher than the actual experimental dipole moments [23]. Furthermore, quantum chemistry approaches often produce an exaggerated electron distribution in molecules, making them more polar than they are in reality [23]. Another reason is that experimental methods take into account solvent and environmental influences (solvent-solvent interaction), whereas ab initio calculations only provide results for a free solute molecule in vacuum [53-55].

The other calculated parameters that are very important in quantum chemistry are the HOMO-LUMO energy gaps of the compounds which reflect the chemical activity of the molecules. Both HOMO and LUMO are the main orbitals that take part in chemical stability. A molecule with large HOMO-LUMO gaps is generally stable and unreactive, while ones with small gaps are generally reactive. The HOMO-LUMO band gap for NIC is 0.169 eV. A difference in electronic distribution was also noticed on the HOMO-LUMO molecular orbital plot of NIC as shown in Fig. 8 (a). Higher electronic distribution was observed at the LUMO orbital level, and this also confirms that the excited states of the molecules have higher dipole moments. The obtained results are also similar the the results reported previously [51,52].
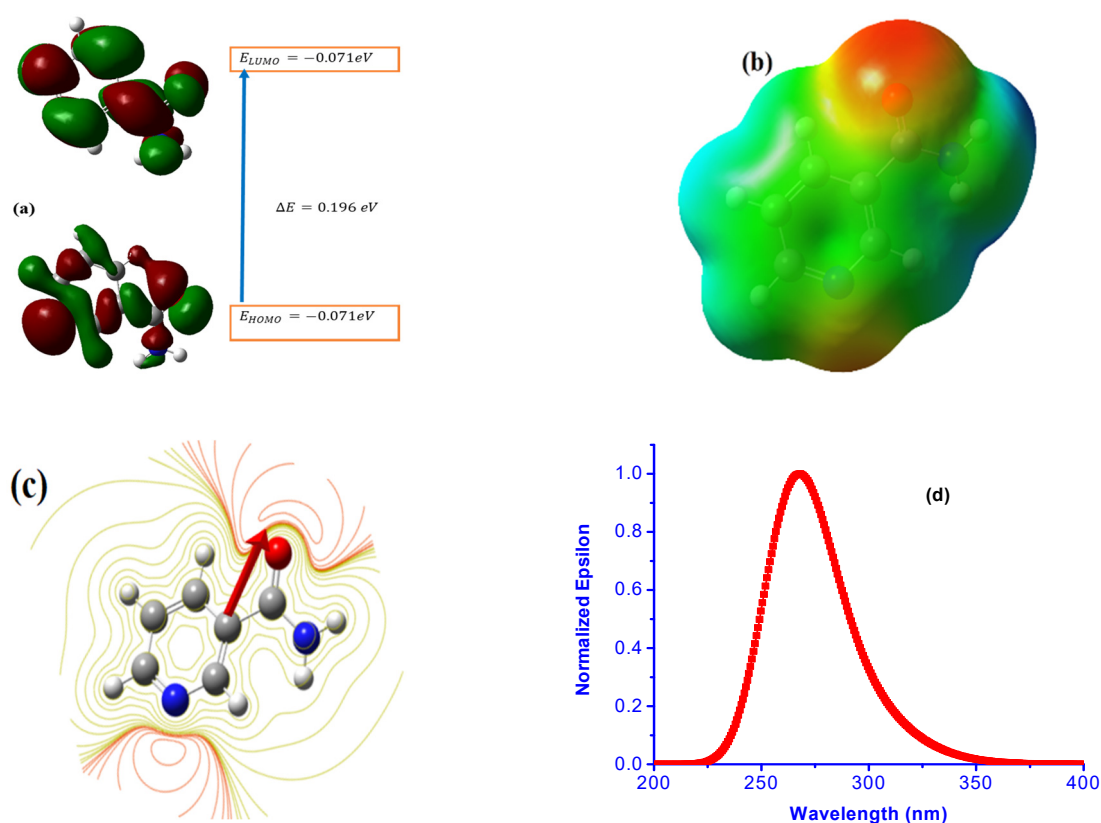
Figure 8. (a) Electron distribution of HOMO and LUMO energy levels; (b) the 3D total electron density with electrostatic potential map (TED-ESP); (c) The 2D electrostatic potential maps around the molecule of NIC and direction of its dipole; (d) Absorbance spectra of NIC with $\lambda_{max} = 268 nm$ theoretically using the Density Functional Theory at B3LYP level of theory at 6-311G**

The electrostatic potential map plot of NIC, as illustrated in Figs. 8(b&c), allows the nucleophilic and electrophilic areas of the molecules to be estimated. Identifying these nucleophilic and electrophilic areas is critical for the design of nonlinear optical materials [56] and helps prediction of the site of attack in various photochemical processes [23,55]. The electrostatic potential map of NIC is represented in red and blue colours. The blue colour represents a positive phase that corresponds to a nucleophilic region and the red colour represents a negative phase that corresponds to an electrophilic region [55,57]. Oxygen creates an electron-rich region and the lowest electrostatic potential of the molecule, and nitrogen is relatively electron deficient for NIC molecules. In addition, the UV/Vis absorption spectra in Fig. 8 (d), the excitation energies, and their corresponding oscillator strengths are determined using TD-SCF-DFT-B3LYP-6-311G** since it determines these better than other methods [55,58,59]. The numerical values are shown in Table 4.

Table 4. HOMO-LUMO energy band gap, UV/Vis. absorption wavelengths and corresponding oscillator strengths determined using TDSCF-DFT-B3LYP-6-311G for Nicotinamide

Band Gap (eV)	λ_1(nm)	λ_3(nm)	λ_3(nm)	E_1(eV)	E_2(eV)	E_3(eV)	S_1	S_2	S_3
0.196	300.75	270.99	265.85	4.1225	4.5753	4.6637	0.0006	0.0042	0.0043

E_1: excited state 1 energy and corresponding wavelength, λ_1; oscillator strength, S_1. E_2: excited state 2 energy and corresponding wavelength, λ_2; oscillator strength, S_2. E_3: excited state 3 energy and corresponding wavelength, λ_3 and oscillator strength, S_3.

CONCLUSION

The ground-state and excited-state dipole moments of nicotinamide were investigated by both experimental and theoretical methods. It was observed that the excited state possessed a higher dipole moment than the ground state. This result confirms that the excited states of nicotinamide are more polarized than their ground state and therefore more sensitive to solvent effects. The differences in the ground state and the excited state dipole moments obtained from various equations are due to the different assumptions and simplifications made in the solvatochromic methods. The ground- and excited-state dipole moments obtained by quantum chemical computation (DFT) provided higher results than experimental findings because the results were computed in vacuum rather than using solvents. In addition, a difference in electronic distribution was also noticed on the HOMO-LUMO molecular orbital plots of NIC. In general, the spectral properties observed, the values of dipole moments, and electronic structures of NIC in different solvents provide important information about charge distribution and solute-solvent interactions, which may be useful in the study of these molecules in biological systems.

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ВПЛИВ ПОЛЯРНОСТІ РОЗЧИННИКА НА СПЕКТРИ ПОГЛИНАННЯ ТА ФЛУОРЕСЦЕНЦІЇ НІКОТИНАМІДУ: ВИЗНАЧЕННЯ ДИПОЛЬНИХ МОМЕНТІВ ОСНОВНОГО ТА ЗБУДЖЕНОГО СТАНІВ

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У цьому дослідженні дипольні моменти основного та збудженого станів нікотинаміду (NIC) були оцінені за допомогою сольватохромних ефектів і комп'ютерних обчислень. Подано загальний огляд впливу розчинників на електронні спектри поглинання та флуоресценції NIC. В обох спектрах спостерігалися виражені сольватохромні ефекти, а зсув піків випромінювання був більшим, ніж у відповідних спектрах поглинання. Експериментальні дипольні моменти основного $\left(\mu_g\right)$ та збудженого $\left(\mu_e\right)$ станів NIC оцінюються за сольватохромними зсувами спектрів поглинання та флуоресценції. Відмінності між дипольними моментами збудженого та основного станів, визначеними всіма методами, досить схожі. Розраховані енергетичні заборонені зони HOMO-LUMO, які становлять 5,566 еВ. Виявлено, що дипольний момент збудженого стану вищий, ніж у основного стану для всіх використаних методів, і це пояснюється більш полярним збудженим станом NIC. Нарешті, спостережувані спектральні властивості, виміряні значення дипольних моментів та електронні структури NIC у різних розчинниках надають важливі відомості про розподіл заряду та взаємодію між розчиненою речовиною та розчинником, що може бути корисним у дослідженні цих молекул у біологічних системах.

Ключові слова: метод сольватохромного зсуву, дипольні моменти основного стану, дипольні моменти збудженого стану, нікотинамід