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Theoretical Study of the Structural and Electronic Properties of NIPAM Polymer Dosimetry Gel

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ABSTRACT: ***Background:*** *Gel dosimeters consist of two types: Frick and Polymer, with compounds that are highly reactive to radiation.* ***Objective:*** *The difference in energy between the Highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) was investigated.* ***Methods:*** *An examination of the structure of a dosimetry gel polymer of type N-isopropylacrylamide (NIPAM) was carried out with the assistance of the Gaussian 09 software, the Fourier Transform Infrared Spectrometer (FTIR), the proton and carbon nuclear magnetic resonance (H NMR-C NMR), and the ultraviolet-visible spectroscopy (UV-vis) approach were used. The molecular geometry was determined using density functional theory (DFT) (B3LYP) and computational means. Subsequently, this molecule's vibrational frequencies and electrical characteristics were examined, with the ground state represented by the 6-31G basis. The computations of the structure, as well as the vibrational frequencies and chemical shift, demonstrated a satisfactory theoretical approximation.* ***Results:*** *Based on the findings, it has been shown that NIPAM has a high-water solubility and is of great assistance in the process of introducing a powerful polar amide group into a hydrophobic polymer via the use of suspension or emulsion polymerization, and strong coupling effect (interaction of magnetic fields) between the hydrogen atoms and the deformation.* ***Conclusions:*** *The atoms within the structure, the molecule is highly reactive, the computed results demonstrated the accuracy of the theoretical approximation despite these discrepancies.*

KEYWORDS: *DFT; Polymer gel; HOMO and LUMO; Dosimetry gel; N-isopropylacrylamide*

INTRODUCTION

Hydrogels "soft and wet" nature has piqued attention widely in various scientific domains [1]–[3]. Gel dosimeters consist of two types: Frick and Polymer, with compounds that are highly reactive to radiation. These gels experience basic modifications in their characteristics depending on the amount of absorbed radiation if subjected to ionizing radiation. The impact of ionizing radiation had previously been addressed well when polymer devices for using radiation dosimetry had initially been established [4]. Nowadays, numerous kinds of gel dosimeters are available worldwide [5], and choosing a gel recipe requires thoughtful evaluation of several factors, such as how far the gel's radiological characteristics are similar to that of water [6]. NIPAM for short with a chemical structure ($C_6H_{11}NO$) with density, is a synthetic polymer that finds widespread use in a wide range of scientific and industrial applications.

NIPAM has good water solubility and useful in introducing a strong polar amide group (that consists of a carbonyl group (C=O) bonded to a nitrogen atom (N)) into a hydrophobic polymer via suspension or emulsion polymerization [7]. As temperature fluctuations affect its characteristics it dissolves in water at a critical temperature below 32°C and does not dissolve above this temperature.

The most important applications include use in medical (drug delivery systems, purification, etc.) and pharmaceutical materials as well as in tissue culture media.

A study is currently in progress to explore the main properties of NIPAM gel to give a good picture of its applicability in different fields as a molecule's chemical and physical characteristics can be greatly impacted by the existence of a group of amides. The investigation includes studying the occupied and unoccupied levels by electron (HOMO-LUMO) and the results of the energy gap. The nuclear magnetic resonance of protons and carbon atoms will be studied for information on the structure by chemical shifting. Moreover, the UV-Vis spectrum gives good information on the gel structure. The structural and electronic properties study of this polymer will be done by using the Gaussian 09 program with density functional theory.

MATERIALS AND METHODS

In recent years, there has been a growing popularity of computational methods for understanding and forecasting molecular activity. Consequently, it is possible to predict molecular activity without conducting experiments. In the current case, one of the theoretical computations, DFT, originally applied to chemistry using numerical approaches known as "muffin tin" or scattered-wave [8] , provides details about many attributes that cannot be obtained empirically and supports experimental evidence [9]. The GAUSSIAN-09W computer program was used for all calculations [10] and Gauss View 5 molecular visualization programs [11]. One of the oldest and most popular exchange-correlation functions [12], the B3LYP hybrid functional, incorporates Lee, Yang, and Parr's correlation functional as well as Becke's three-parameter exchange functional in the DFT calculations.

RESULTS AND DISCUSSION

The Structure of Molecules

Utilizing the starting point set 6-31G plus the DFT approach, the geometric optimization of the molecule, Figure 1, its geometric parameters, and energy values were determined [13]. NMR, UV, and IR spectra were theoretically calculated from optimized geometry using a similar method and basis set. The gauge-independent atomic orbital (GIAO) approach was used to obtain the compounds' NMR chemical shift values.

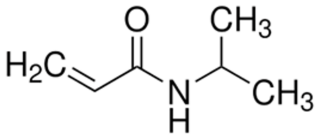

Figure 1. N- Isopropylacrylamides ($C_6H_{11}NO$)

The location and structure of molecules change, affecting not only their energy as well as their physical features. Geometric optimization yields approximately the structure of a highly stable molecule, approximately. Consequently, the structure of the unstable, low-energy molecule is found. The theoretical geometric structure of NIPAM is shown in Figure 2 after all necessary computations have been completed into just one component [14].

Figure 2. Theoretical optimization of the NIPAM molecular structure

HOMO-LUMO Analysis and Electronic Properties

The most commonly recognized quantum chemical characteristics are the highest occupied molecular orbital (HOMO) (30 orbitals) and lowest unoccupied molecular orbital (LUMO) (60 orbitals) energies. Such orbits that are also known as frontier molecular orbitals are essential for figuring out a molecule's optical and electrical characteristics, especially in chemical processes [15]. The HOMO and LUMO surfaces and energies of the examined structure are shown in Figure 3. A molecule's capacity to provide electrons is measured by its HOMO energy, which is correlated with its ionization potential. Furthermore, LUMO energy, which is directly related to electron affinity and has the values E HOMO = -18.615 Hartree (506.54 eV) and E LUMO = -0.00320 Hartree (0.087 eV), represents a molecule's capacity for gaining electrons comparing with [16].

The chemical stability of a molecule can be determined by measuring the difference in energy between its HOMO and LUMO orbitals. Figure 3 shows that there's a significant energy differential between HOMO and LUMO. The molecule appears to be in an unstable state given the breadth of that energy range. Chemical potential($C_{\mathfrak{p}} = -\chi$), chemical hardness($\eta = \frac{IP+EA}{2}$), chemical softness ($S = -\frac{1}{\eta}$), and electronegativity ($\chi = \frac{IP+EA}{2}$) were also calculated using the HOMO and LUMO energies. These compounds' electrical properties are listed in Table 1 which illustrates the molecule's exceptional stability, which includes low chemical reactivity and high energetic stability [17].

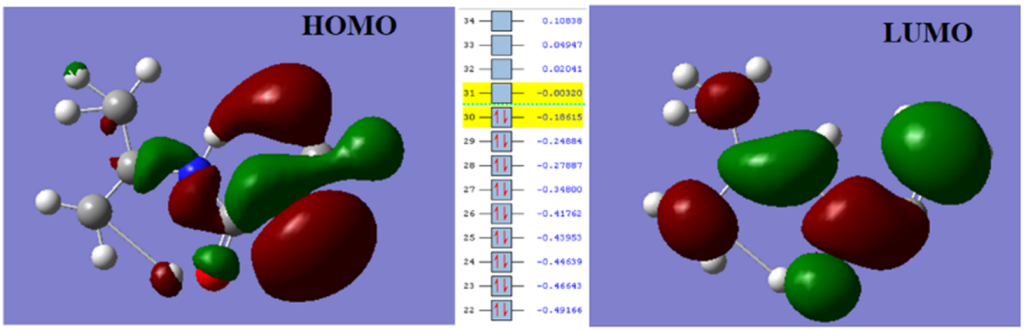

Figure 3. 3D representation iso-surface of HOMO / LUMO orbitals of the geometry optimized using hybrid DFT (B3LYP) indicating significant LUMO electron density

Table 1. Dosimeter gel NIPAM molecule geometric parameters of electronic structure using B3LYP and 6-31G

Geometric parameter	Value in eV	Geometric parameter	Value in eV
E- Homo	−506.54	η- hardness	2.994
E- LUMO	−0.087	s- softness	0.158
ΔE- Energy gap	5.148	w- Electrophilic index	2.041
A- Electron affinity	0.547	μ- potential	−4.001
χ- Electronegativity	3.471	-	-

Table 1 displayed specific geometrical parameters of a molecule. The bond lengths for C=C and C-C in a ring are 1.4336 and 1.3819 Å, respectively, while the bond length for C-C in a chine is 1.5084 Å. Additionally, the bond length in a plane is 1.0870 Å for C-H and 0.9770 Å for O-H. For C-N, C-O, and C=O, the bond lengths are 1.3558, 1.3839, and 1.2586 Å, respectively [18], [19]. Because of the extremely high angle across the atoms within the structure, the molecule is highly reactive.

NMR Analysis

Nuclear magnetic resonance spectra of hydrogen (H NMR) are a vital technique for characterizing and analyzing material specimens as well as doing investigations into the structure of materials, and all compounds [20], [21]. The NMR chemical shift calculations in this molecular structure were done theoretically using the Gauge-Including Atomic Orbitals NMR attitude and the 6-31G base set in the DFT for NIPAM gel as in Figure 4 comparing with the experimental [22]. Since the density of

electrons around protons leads to the expected effect of attenuation, we find that aromatic protons show different ranges of chemical shifts, as electronegative groups are arranged to minimize the density of electrons around the proton. This test can provide information about the proton proximity (i.e., atoms bound by three bonds).

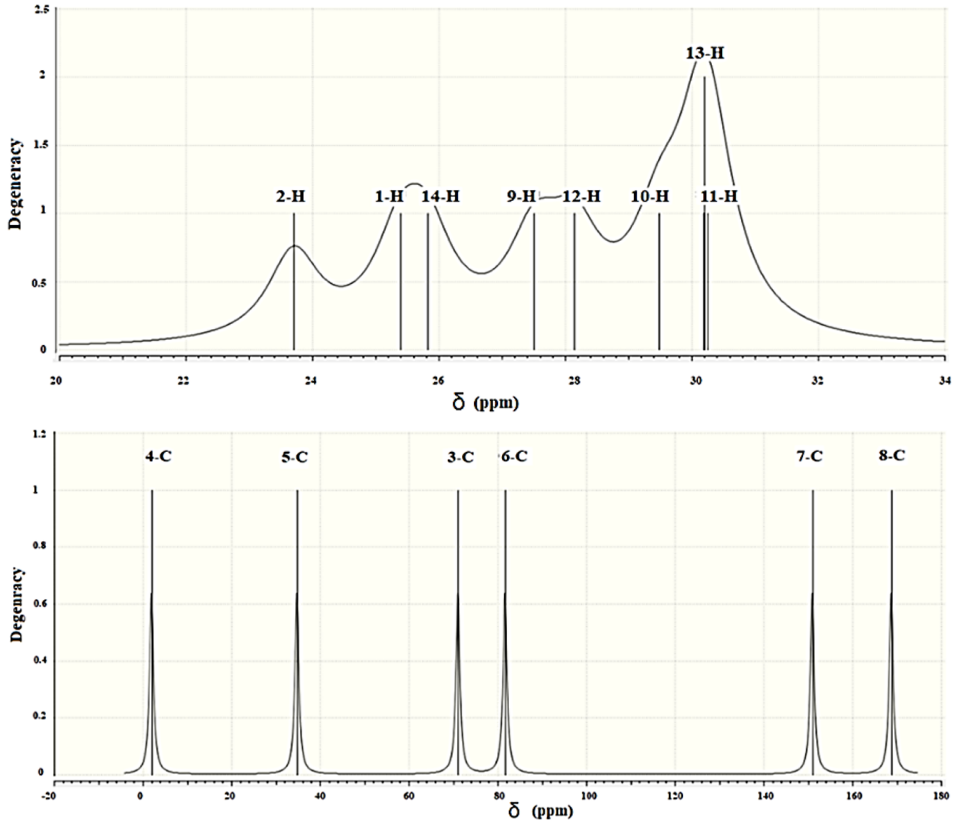

Figure 4. The H NMR and C NMR spectrum

It can be seen from Figure 4 that there is one (singlet) proton peak resulting from the lack of neighboring hydrogen atoms. The two double peaks (equal in size - double) were obtained as a result of the interaction of its magnetic field with the field of (N) neighboring non-equivalent hydrogen (as the peak splits into N+1). The diagram also shows the strong coupling effect (interaction of magnetic fields) between the hydrogen atoms and the deformation of the last two peaks, which occurs when one circuit element, interacts with another through the electromagnetic field. This interaction results in the transfer of energy between the two elements, which affects the operation of the integrated circuits, where the parts of the peak closest to each other become larger while the outer parts appear smaller (known as roofing). As for why there is a broad peak in the proton spectrum, it appears for a molecule with exchangeable protons at (-NH), which is true for peaks with multiplicity.

For carbon, it is much easier to analyze because the carbon less bonding. The number of peaks equals to the number of protons attached to carbon from the hydrogen atoms. The spectrum shows the peaks represented in points that depend on the type of atoms that carbon bonded. As the electronegative is high for NIPAM, the shifting is high, then the chemical shifting towered the weak field and the displacement is great. The spectrum will simply ever display a connection between carbon and protons—never between two carbons.

UV-Vis Absorption Analysis

It is a very important simple method used to test the molecule structure changes and formation [23], [24]. NIPAM's UV-vis spectroscopy was examined to have the absorbance as attenuation of the beam. UV-vis theoretical computations were carried out with a 6-31G basis set using DFT/B3LYP [25]. Figure 5 displays the theoretically estimated UV-Vis spectra of NIPAM. The UV-vis spectrum was obtained between 250 and 450 nm, which can be compared with that of organic molecules 200nm and

400nm) [26], [27] and the peak had a Gaussian band shape. The technique most commonly employed for forecasting electrically excited states and interpreting UV-Vis spectra is the DFT method. The electrons of atoms will excite when the energy is absorbed also the atoms can vibrate and rotate around each other, which means it has a level density that is considered packed on the electronic level. In this instance, oscillator strengths, vertical excitation energy, and wavelengths of our computed results of the title molecule were determined using the DFT. At $\lambda_{max} = 32nm$, the significant absorption maxima were found to reflect the size of the chromophore and absorbance of the light when strikes the chromophore.

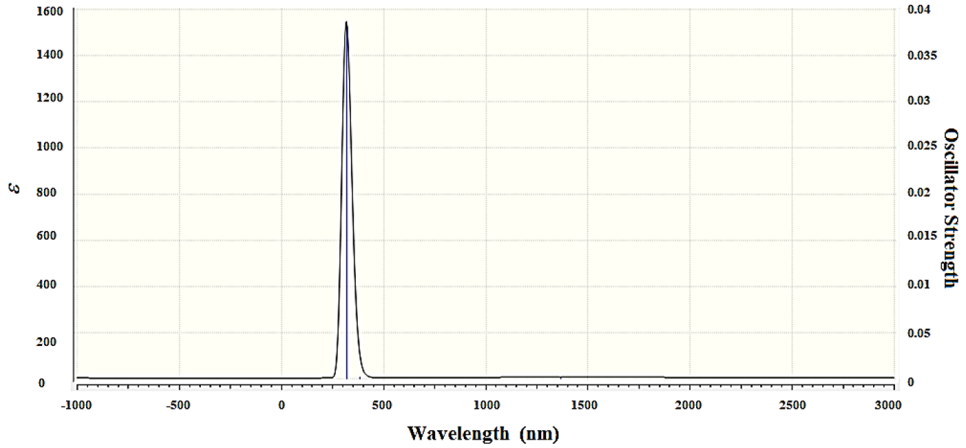

Figure 5. UV-vis spectrum of NIPAM dosimetry gel molecule

Vibrational Frequencies

The vibrational energy levels associated with chemical bonds in a sample are measured using IR spectroscopy, one of the spectroscopic methods. The peaks in the IR spectra correspond to specific vibrations of chemical bonds or functional groups inside molecules [1]. The structure of NIPAM was determined by IR spectroscopy in the region of 3250-250 cm^{-1} as narrow bands and was shown in Figure 6.

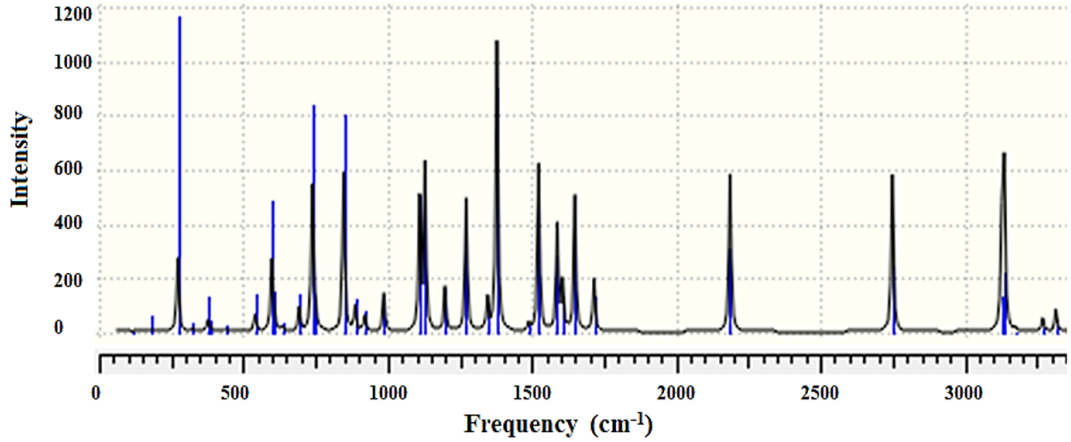

Figure 6. IR Spectrum for NIPAM diametric gel molecule

The two strong bands at 250 nm and 1370 nm were due to the carbonyl group of the amid comparing with the experimental value 1640 cm^{-1} (6980 nm) [28]. Three types of bands can be seen in the figure: strong (covers most of the intensity), medium (falls to about half intensity), and weak (one-third or less intensity). The molecule has characteristic absorption peaks; the band at 250 cm^{-1} and 1380 cm^{-1} are determined to the stretch for the carbon-bonded (C=O) as strongly polar bonds a stretching vibration and possible triple bond of C-C, and medium bonds at 2470 nm (N-H) compare

with 1543 cm^{-1} (3458 nm) [29]. The remaining bands be weak (C-H). However, utilizing a single unit in computations and viewing electron correlations as partial helps explain the discrepancies between theoretical and actual data (particularly N-H stretching vibration and C-H aliphatic stretching states).

CONCLUSION

Using IR, UV-Vis, H NMR, and C NMR , the structural and spectroscopic characteristics of the NIPAM molecule were ascertained. The B3LYP/6-31G level was used in this investigation to calculate the molecular structure, vibrational frequencies, and chemical shift values. The electronic absorption spectra were calculated using the DFT approach. An isolated single gas phase molecule was used for the computations. NIPAM has a high-water solubility and is of great assistance in the process of introducing a powerful polar amide group into a hydrophobic polymer via the use of suspension or emulsion polymerization, and strong coupling effect (interaction of magnetic fields) between the hydrogen atoms and the deformation. Also, the atoms within the structure and the molecule are highly reactive, and the computed results demonstrated the accuracy of the theoretical approximation despite these discrepancies.

SUPPLEMENTARY MATERIAL

None.

AUTHOR CONTRIBUTIONS

Swait S. Mohammed: Resources, data curation and writing original draft preparation. Israa F. Al-Sharuee: Writing review, editing, visualization, supervision, and project administration. Akram Mohammed Ali: Conceptualization, methodology, and software. Adil Elrayah: Final reading and review of references and figures.

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None.

DATA AVAILABILITY STATEMENT

None.

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CONFLICTS OF INTEREST

The authors declare no conflicts of interest.

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