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Theoretical analysis of ADP molecule in gas phase and aqueous solution: a DFT and PCM/TD-DFT study

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Abstract: This paper has reported some theoretical results for the geometry optimization in ground state (S0) and the first excited state (S1), the frontier molecular orbitals, the global chemical reactivity descriptor, the excited states, the absorption and emission spectra in gas phase and aqueous solution of protonated Adenosine diphosphate molecule. Also, the excited state intramolecular proton transfer process was reported between O37-H38···N13 bonds. Then, the results obtained have been compared with the experimental data reported and, therefore, available in literature. All calculations were carried out using density functional theory and time-dependent density functional theory method with B3LYP functional with 6-311+G (d, p) basis set. As well as, the solvent effects were investigated using Polarizable Continuum Model. As a conclusion, it has been indicated that the theoretical results obtained in this work are all in well agreement with experimental counterparts taken from literature.

Keywords: *ADP, PCM/TD-DFT, Excited states, Absorption, Emission*

Highlights

- *ADP molecule has been investigated as theoretical in gas phase and aqueous solution.*
- *The first ten excited states of ADP molecule have been calculated using DFT and TD-DFT.*
- *HOMO, LUMO and HOMO-LUMO energy gap have been calculated in details.*
- *Chemical hardness, electronic chemical potential, electronegativity, electrophilicity investigated*
- *Absorption and emission spectra of ADP molecule has been calculated theoretical in gas phase and aqueous solution.*

1. Introduction

Adenosine diphosphate (ADP) is an important organic compound that is essential to the flow of energy in living cells. In addition, it plays a central role in fundamental biological reactions catalyzed by some enzymes such as ATPases and kinases [1]. It is formed by three important structural components that a sugar attached to adenine and two phosphate groups. The high energy phosphate bonds of ADP molecule have attracted a worldwide attention due to many theoretical [2-6] and experimental [7-12] studies due to their importance in energy storage and energy transfer in biological systems. However, a clear statement has not yet emerged that some phosphate compounds contain energy more than ordinary ester phosphates. We hope that this uncertainty can contribute to examining the excited states of ADP molecule in both gas phase and aqueous solution.

The process of absorption of biomolecules such as ADP may has some important causes such as mutations and bond breaks, and these processes can lead to photo chemical and photo physical events. These photo-induced processes can be explained by examining the excited states of molecules [13]. To understand and interpret the static and dynamic behaviors of biomolecules in excited states,

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molecules in excited states should be examined as both experimentally and theoretically [14-19]. Especially, studies on molecules in gas phase gives detailed information about electronic structure of molecule in excited states. However, it may still be a need for the results obtained to be checked by taking environmental conditions into account, Because many of the biological processes are known to occur in vivo and in vitro [20]. The studies for molecules in aqueous solution show influence of excited state and structural features [21]. ADP molecule is a fragment from ATP in as negative radical and we have add H atom twice to be protonated, this state after protonation process can change the all properties of ADP molecules. Experimentally, it cannot be determined where the proton was attached; however it can be determined using quantum chemical calculations. In these calculations, density functional theory (DFT) method has been broadly used in physics, chemistry, biology and materials science. DFT method successfully predicts structure and properties of ground state. In addition, TD-DFT method is successfully used to calculated excited states of molecules.

Due to the biological significance of ADP molecule, many quantum mechanical studies were carried out for understanding reactions. Particularly, the associative and dissociative mechanisms molecule in hydrolysis process have been investigated with DFT and HF methods [6, 22, 23]. These mechanisms have also been studied in the presence of Mg ions bound to negatively charged oxygens at phosphate group [24]. The interaction of ADP molecule with various metals such as Al+3 has been studied by using NMR spectra experimentally and theoretically [25, 26]. The photoelectron spectra and infrared multiple photon dissociation spectra as well as free hydration energies of doubly deprotonated ADP dianions have been obtained in gas phase [27-29]. In addition, fragmentation patterns of ADP anions and dianions have been obtained experimentally [30]. The XRD study of molecule has been studied by several groups [31, 32]. As a result of these studies, it has been observed that the structure of ADP molecule presents some adenine bent towards some phosphate group, as i have obtained with this work. Also, the absorption and luminescence spectra of ADP molecule obtained experimentally were wanted to be examined by courtesy of X-ray spectroscopy. However, spectra could not be obtained due to the decomposition of the molecule in temperature transitions [33].

In presented study, ADP molecule neutralized by adding one hydrogen atom was reported the ground state structure and excited states both in gas phase and in aqueous solution. As well as, the frontier molecular orbitals, the Global chemical reactivity descriptor, absorption and emission spectra, electronic transition energies and corresponding oscillation strengths of electronically excited states for ADP molecule were reported using time dependent density functional theory (TDDFT) and polarizable continuum model (PCM-TDDFT) methods. It has been given by combining the obtained theoretical results with experimental data reported in literature. Such studies will be helpful for theoretical modeling of ionic compounds and thus will contribute to reducing differences between experimental x-ray spectra and theoretical studies [34]. Another important use of such a study will contribute to mass spectrometry studies for molecular weight and ordering of charged bio molecules [35].

2. Computational Method

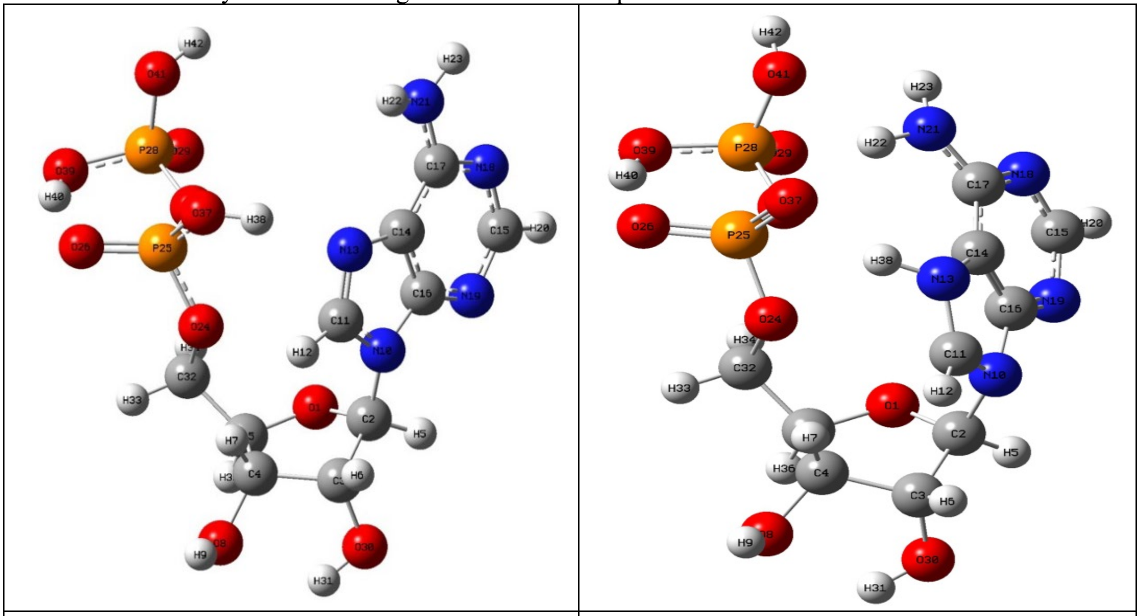
All calculations have been carried out by Gaussian 09 package program [36]. Density functional theory (DFT) has been used to optimize the ground state electronic structure of ADP molecules, and Time dependent density functional theory (TDDFT) has been used to optimize the excited state structure. The TDDFT method has been verified to be a very useful tool to effectively describe the excited states. All calculations have been performed using Becke's three-parameters hybrid exchange functional with Lee−Yang−Parr gradient-corrected correlation (B3LYP functional) and B3LYP / 6-31+G (d,p) basis set [37, 38]. The Polarizable Continuum Model (PCM) has been used to examine the effect of the solution on the molecule. PCM has been already shown to provide a reliable treatment for biological molecules [39].

3. Results and discussion

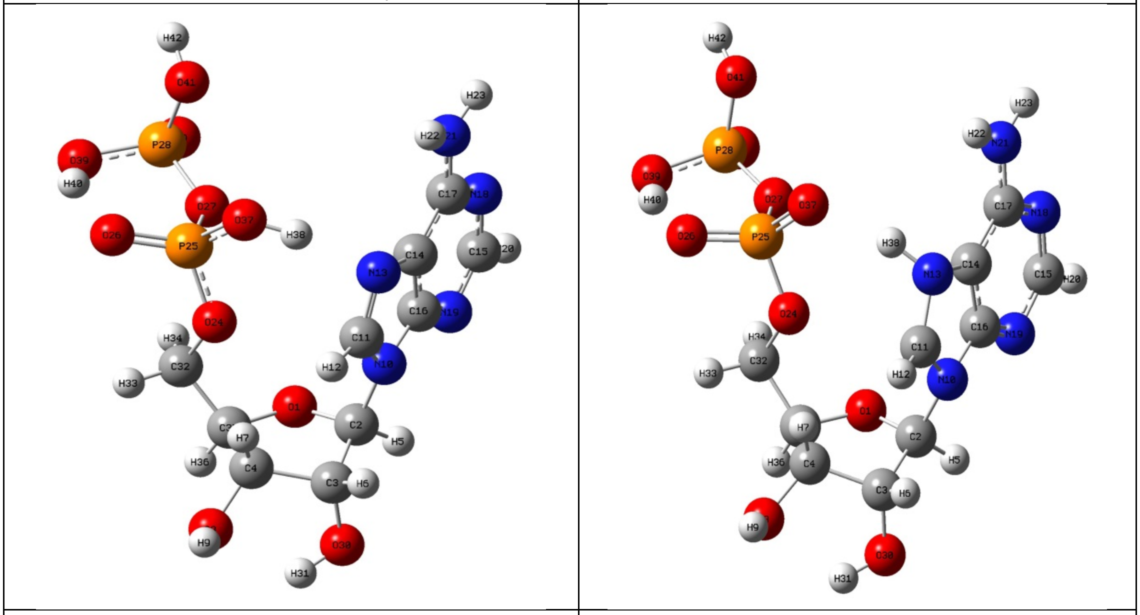
3.1. Optimized geometric structures

The optimized structures of the protonated ADP molecule have been obtained using the

DFT/B3LYP method for the ground state and TDDFT/B3LYP method for the excite state. The optimized geometrical structures and parameters are shown in Figure 1 and listed in Table 1, respectively. The results obtained have shown that the structure of ADP molecule has been look like a u-shape by bending towards the phosphate group of the adenine base. The structure of the molecule obtained theoretically shows a well agreement with obtained structure in the XRD study. The obtained ground state geometry parameters of ADP molecule have been compared with XRD results [40]. As listed in Table 1, the results have been found to be quite well agreement with the ground state structures in both gas phase and aqueous solution conditions. However, the structures in the excited state have not been compared because of absence of experimental data.



ADP Gas Phase S$_0$ | ADP Gas Phase S$_1$



ADP Aqueous Solution S$_0$ | ADP Aqueous Solution S$_1$

Figure 1. Optimized geometric structures in the ground state (S$_0$) and the first excited state (S$_1$) for the ADP molecule in gas phase and aqueous solution.

The lengths of O37-H38 and H38-N13 bonds of the gas phase molecule obtained in the ground state have been calculated to be 1.00 Å and 1.79 Å, respectively. The ground state structure lengths of the same bonds in aqueous solution have been calculated as 1.01 Å and 1.73 Å and given in Table 1. These results can show that the proton transfer process can occur. If the ground state and excited state structures in both environments are compared carefully, one can see intramolecular proton transfer or hydrogen atom displacement. Also, after proton transfer proses, the P25-O37 bond length shortens from 1.574 Å (S_0) to 1.517 Å (S_1) in gas phase and from 1.571Å (S_0) to 1.504 Å (S_1) in aqueous solution. However, the N13-C11 bond length stretches from 1.316 Å (S_0) to 1.406 Å (S_1) in gas phase and from 1.318 Å (S_0) to 1.423 Å (S_1) in aqueous solution.

Table 1 Selected theoretical and XRD geometrical parameters (bond lengths in Å, Dihedral Angles and bond angles in degrees) by the DFT/B3LYP/6-31+G (d,p) for the ADP molecule in gas phase and Aqueous Solution

Bond Length Å	**XRD [40]**	**Gas phase (S_0)**	**Gas phase (S_1)**	**Aqueous solution (S_0)**	**Aqueous solution (S_1)**
N18-C15	1.34	1.343	1.334	1.34274	1.31392
N18-C17	1.34	1.344	1.356	1.35082	1.36975
C16-N10	1.38	1.393	1.34687	1.39126	1.39985
C14-C17	1.41	1.411	1.40557	1.41353	1.41107
C14-N13	1.40	1.391	1.41619	1.39146	1.39571
C2-O1	1.39	1.419	1.41827	1.42269	1.42609
C2-C3	1.54	1.537	1.53282	1.53332	1.53145
C3-O30	1.40	1.411	1.41372	1.41754	1.41964
C4-O8	1.41	1.42695	1.42730	1.42314	1.42433
C32-O24	1.44	1.44988	1.43824	1.45806	1.43835
O24-P25	1.59	1.60630	1.62824	1.59152	1.61643
P25-O37	1.53	1.574	1.51740	1.57183	1.50460
P25-O26	1.50	1.490	1.50307	1.49374	1.51845
P25-O27	1.65	1.624	1.68744	1.64180	1.69186
P28-O29	1.52	1.473	1.47664	1.47985	1.48628
P28-O39	1.57	1.582	1.58727	1.59461	1.59431
N13-C11	1.38	1.31661	1.40661	1.31880	1.42373
Bond Angles (°)					
C15-N19-C16	108	111.61	114.31048	111.60730	114.42095
N19-C16-N10	124	127.71	125.38535	127.79033	126.25508
C14-C16-N10	104	105.64	109.90169	105.74704	108.92301
C16-C14-C17	118	116.25	116.05711	116.66949	116.01123
C14-N13-C11	103	104.15	102.26086	104.36137	103.34031
C2-N10-C11	124	127.33	122.47130	127.70140	125.40432
C2-O1-C35	108	112.14	112.30510	111.66457	111.80979
O8-C4-C35	109	109.45	109.77026	109.38410	109.47966
C3-C4-C35	103	103.86	103.25431	103.83362	103.57615
O1-C35-C4	108	106.87	105.80431	106.82882	106.28787
O26-P25-O37	118.6	114.60	122.95329	114.12974	121.82637
O27-P25- O37	108.5	108.13	106.73519	107.32326	108.43626
O27-P25- O26	109.1	111.29	107.04266	110.12240	105.82772
P25-O27-P28	130.6	129.28	128.16134	128.43378	128.46656
O39-P28- O29	117.9	118.04	115.94217	113.60920	113.81233
O39-P28-O27	103.9	104.03	105.79997	105.36065	105.72332
O29-P28-O27	113.5	111.27	115.03330	113.05390	114.15639
O41-P28-O27	103.4	102.50	98.50969	99.06392	100.14702
C32-O24-P25	123.2	123.17	121.88382	124.18251	123.80948
Dihedral Angles (°)					
C4-C35-C32-O24	57	51.06	55.00175	53.86332	57.09252
C35-C32-O24-P25	148	166.24	159.00677	167.34074	178.04348
C32-O24-P25-O37	-179	-173.46	-171.64773	-177.40538	-178.04141

3.2. Frontier molecular orbitals (FMOs) and Global chemical reactivity descriptor

The frontier molecular orbitals (FMOs) of ADP molecular have been calculated using DFT/B3LYP/6-31+G (d,p) method. The molecular orbitals structures in both gas phase and solution form have been shown in figure 2. The FMOs are comprised of (HOMO) highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The HOMO-LUMO Gap energy is the difference in energy between the HOMO and the LUMO. The FMOs are important parameters in describing the chemical reactivity and interaction of molecule. Also, it can provide insights in nature of the electronically excited state. The global chemical reactivity descriptor for example ionization potential (I), electron affinity (A), chemical hardness (η), chemical softness (S), electronic chemical potential (μ), global electrophilicity index (ω) are used to predict the reactivity and stability of molecules. These descriptors have been calculated using equations (1), (2), (3) and (4), respectively.

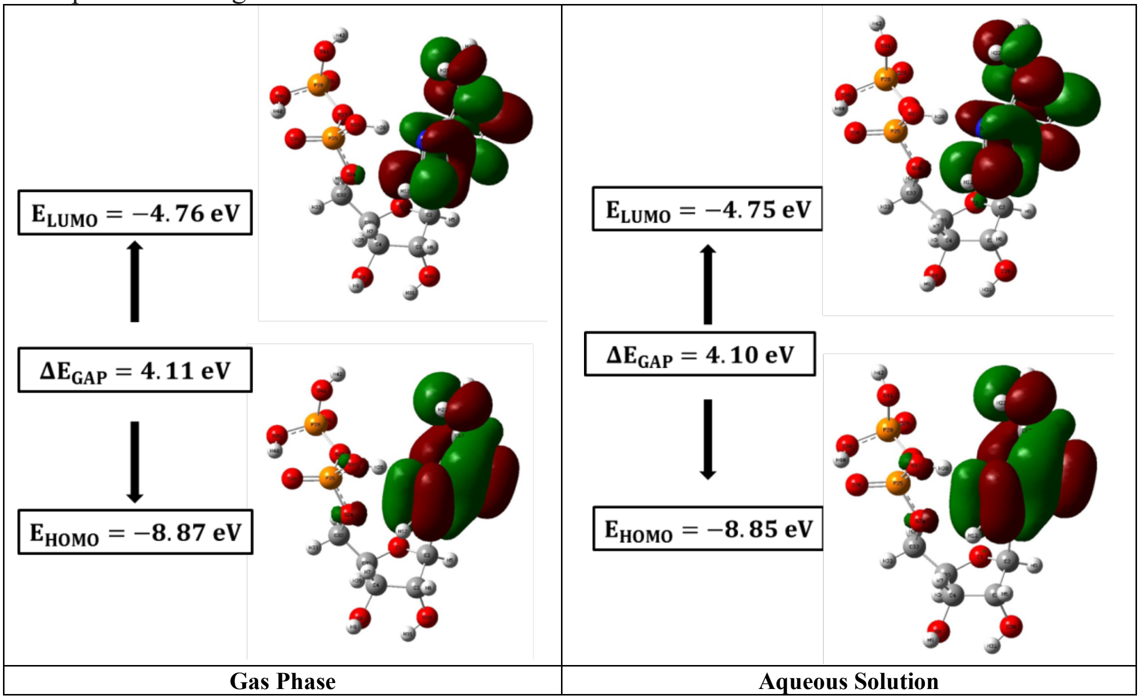


Figure 2. The molecular orbitals and energies for the HOMO and LUMO of the ADP molecule in gas phase and aqueous solution

The obtained gas phase HOMO and LUMO energies are – 8.87 eV and – 4.76 eV respectively, and the energy gap between them is found to be 4.11 eV. Whereas, the obtained aqueous solution HOMO and LUMO energies are -8.85 eV and – 4.75 eV, respectively, and the energy gap between them is found to be 4.10 eV. Since the large energy gap of molecule has higher stability and lower chemical reactivity, the molecule can be concluded to be quite stable.

The global chemical reactivity descriptor for example ionization potential (I), electron affinity (A), chemical hardness (η), chemical softness (S), electronic chemical potential (μ), global electrophilicity index (ω) have been used to predict the reactivity and stability of the molecule. These descriptors have been calculated using the following equations.

$$\eta = \frac{1}{2}(I - A) \qquad (1)$$

$$S = \frac{1}{\eta} \qquad (2)$$

$$\mu = -\frac{1}{2}(I + A) \qquad (3)$$

$$\omega = \frac{\mu^2}{2\eta} \qquad (4)$$

I and A are single electron ionization potential ($I = -E_{HOMO}$) and electron affinity ($A = -E_{LUMO}$) of the molecule, respectively. The global chemical reactivity descriptors have been listed in table 2.

The results have shown that ADP molecule in both gas phase and aqueous solution conditions is kinetically stable with the hardness values. The chemical softness, the chemical potential and the electrophilicity index values have shown that the molecule in both environments possesses chemical strength and stability.

3.3. Excited states

The excited states of molecule have been calculated using TDDFT method for gas phase and PCM-TDDFT method for aqueous solution. The results obtained for gas phase and aqueous solution have been presented in table 3 and 4, respectively. According to results obtained in gas phase and aqueous solution calculations, in the Franck–Condon region the first excited state corresponds to the transition from the highest energy occupied molecular orbital to the lowest energy molecular orbital. This transition corresponding to maximum oscillator strength has been calculated at 258.55 nm. The second excited state corresponds to HOMO-1→LUMO transition and oscillator strength (0.0095).

Table 2. The global chemical reactivity descriptors for ADP molecule in gas phase and aqueous solution.

Chemical Reactivity Descriptor	Gas Phase (eV)	Aqueous Solution (eV)
Electron affinity (A)	4.76	4.75
Ionization energy (I)	8.87	8.85
Chemical hardness (η)	2.055	2.05
Chemical softness (S)	0.486618	0.487804
Electronic chemical potential (μ)	-6.815	-6.8
Global electrophilicity index (ω)	11.30	11.27

Table 3 The vertical excitation energies, wavelength, oscillator strengths and major contributions for ADP molecule in gas phase.

Excited states	Vertical excitation energies (eV)	Wavelengths (nm)	Oscillator strengths	Major contributions
S_1	4.795	258.55	0.1752	HOMO→LUMO (87%)
S_2	4.878	254.12	0.0095	H-1→LUMO (89%)
S_3	5.110	242.62	0.0039	HOMO→L+1(74%) HOMO→L+2 (15%)
S_4	5.219	237.55	0.0239	H-2→LUMO (16%) HOMO→L+1(24%) HOMO→L+2 (53%)
S_5	5.452	227.39	0.001	H-1→L+2 (92%)
S_6	5.510	224.97	0.0128	HOMO→L+3 (84%)
S_7	5.887	210.58	0.0341	H-6→LUMO(14%) HOMO→L+4 (55%)
S_8	5.908	209.85	0.0126	H-6→LUMO (45%) H-1→L+1(20%) HOMO→L+4 (11%)
S_9	5.940	208.705	0.0151	H-1→L+1 (62%)
S_{10}	5.953	208.26	0.1108	H-3→LUMO (15%) H-2→LUMO (43%) H-1→L+1(12%) HOMO→L+4 (11%)

According to the data obtained in aqueous solution calculations, the first excited state corresponds to the transition from HOMO to LUMO. The energy, wavelength and oscillator strength have been determined to be 4.801 eV, 258.19 nm and 0.2462, respectively. The major contribution for this HOMO→LUMO transition is taken place with 90 percentage. Similar to the gas phase, the second excited state for solution corresponds to HOMO-1→LUMO transition. The energy, wavelength and oscillator strength have been to be 5.078 eV, 244.14 nm and 0.0008, respectively. The major contribution for this transition is with 93 percentage. For the other transitions, the energy, wavelength, oscillator strength and major contribution values have been presented in table 3 and table 4.

3.4. Absorption and emission spectra

As shown in the figure 3, the absorption spectrum of ADP in both environments has a very similar pattern and two intense spectral regions. Comparison of the results for both environments has shown that HOMO→LUMO transition dominating spectra is very little affected by the solvent. The excitation energies are 4.79 eV (258.55 nm) for gas phase and 4.80 eV (258.19 nm) for aqueous solution. The second peaks have been observed at 5.95 eV (208.26 nm) for gas phase and 5.94 eV (208.53 nm) for aqueous solution. These transitions corresponds to HOMO-2→LUMO transitions.

Table 4 The vertical excitation energies, wavelength, oscillator strengths and major contributions for ADP molecule in aqueous solution.

Excited states	Vertical excitation energies (eV)	Wavelengths (nm)	Oscillator strengths	Major contributions
S_1	4.801	258.19	0.2462	HOMO→LUMO (90%)
S_2	5.078	244.14	0.0008	H-1→LUMO (93%)
S_3	5.124	241.94	0.0481	H-2→LUMO (15%) HOMO→L+1 (74%)
S_4	5.435	228.09	0.0087	HOMO→L+2 (93%)
S_5	5.582	222.08	0.0026	H-1→L+1 (96%)
S_6	5.869	211.25	0.0309	HOMO→L+3 (14%) HOMO→L+4 (74%)
S_7	5.881	210.80	0.0093	HOMO→L+3 (80%) HOMO->L+4 (13%)
S_8	5.945	208.53	0.1777	H-4→LUMO (14%) H-2→LUMO (65%)
S_9	5.996	206.77	0.0058	HOMO→L+5 (86%)
S_{10}	6.055	204.75	0.0035	H-6→LUMO (82%)

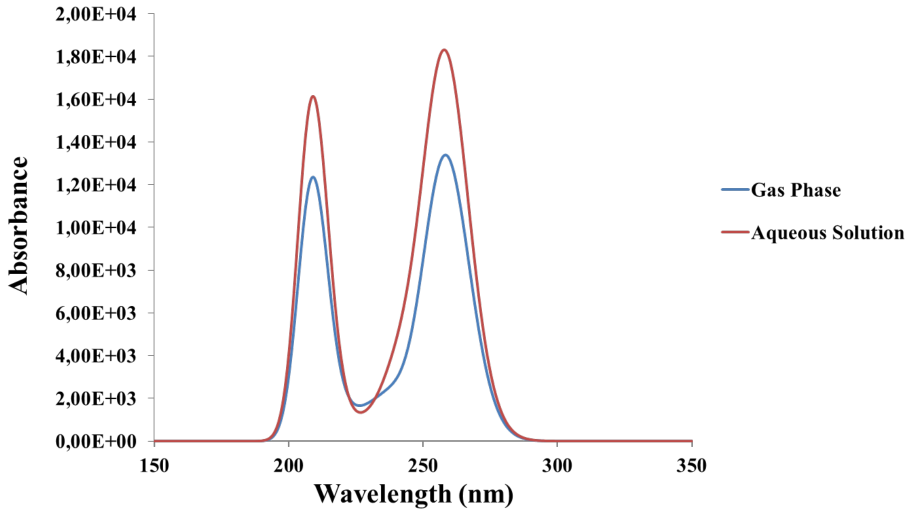


Figure 3. Absorption spectra of the ADP molecule in gas phase and aqueous solution

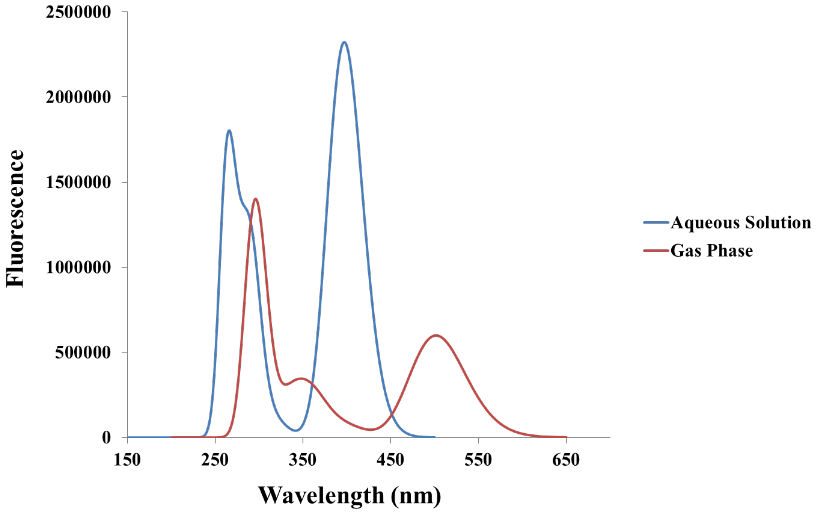


Figure 4. Fluorescence (emission) spectra of the ADP molecule in gas phase and aqueous solution.

The ADP molecule exhibits three peaks in both environments as shown in the figure 4. The first peak of ADP in aqueous solution has been observed at 3.12 eV (396.81 nm) which is associated with HOMO→LUMO transition. The second peak has been observed at 4.69 eV (263.85 nm). This peak corresponds to a HOMO-7→LUMO transition. Finally, the third peak was observed at 4.23 eV (292.78 nm) and corresponds to HOMO-2→LUMO transition. The maximum fluorescence band in ethanol has been obtained at 365 nm in literature [41]. The first peak in gas phase has been observed at 4.20 eV (294.83 nm) which associates with HOMO-6→LUMO transition. The second important transition was observed at 2.47 eV (501.29 nm). This transition has been attributed to HOMO→LUMO. Finally, the third peak has been observed at 3.69 eV (335.88 nm) and attributed to HOMO-4→LUMO transition. In aqueous solution, the emission spectrum has been observed that is significantly blue shifted according to gas phase emission spectrum.

4. Conclusion

In this work, ADP molecule in gas phase and aqueous solution form have been investigated and its prominent properties, such as Structural, Frontier molecular orbitals, exited states, global chemical reactivity descriptor, absorption and emission spectra, have been determined using DFT and PCM/TD-DFT methods. Theoretically calculated three-dimensional chemical structure has shown well agreement with XRD results. Also, the bond length and bond angles obtained for both environments have been found in quite well consistent of XRD results. After ADP molecule is excited, we have realized that a hydrogen atom transfer or a proton transfer occurs between O37-H38···N13 bonds. The molecular orbital analysis has shown that ADP molecule is quite kinetically stable. The calculations for the excited states have shown that it is dominated by HOMO LUMO transition and energy values for gas phase and aqueous solution have been found to be 4.795 eV and 4.801 eV, respectively. We have found that although the absorption spectrum has not much affected in aqueous solution, it has a significant effect on the emission spectrum. We can clearly say that the theoretical studies are important to better understand the specific origins of the minor bands observed in experiments. Also, it can contribute to mass spectroscopy studies for molecular weight and ordering of charged bio molecules.

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